Automotive shredder residue (ASR) for clean energy systems (pyrolysis and gasification) to produce sustainable green energy

by

Ala H. M. Khodier

A thesis submitted in partial fulfilment of the requirements for the degree of MSc (by Research) at the University of Central Lancashire

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Supervisor: Professor Karl S. Williams

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ABSTRACT

One of the major challenges facing the automotive industry is meeting the recycling and recovery targets set by the revised European End-of-life Vehicles directive (which has set a target of 95%wt for recovery from vehicles by 2015). The remaining non-recovered material is 20–25%wt (known as automotive shredder residue (ASR)). It is this material which must be processed to meet the higher targets. Currently, the residue is disposed of, which in many cases is landfill. The option to recover material to meet European target is currently limited to mechanical sorting via post-shredder technologies (PST). Thermal treatments options for ASR in within new emerging waste to energy plants is debatable. This is making it difficult to fully implement the requirements of the directive and the future application of the circular economy package.

This work has investigated the detailed syngas compositions and solid residue (char) characteristics produced from ASR thermal treatment (pyrolysis) in a pilot-scale rotary kiln at 800-1000ºC. The concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and the toxicity levels in the char were determined. New data on critical factors for the processing of char and its subsequent use are presented. In addition, the results of raw ASR (obtained from UK shredder plant) characterisation were used to assess commercial thermal plants from around the world. The assessment study undertaken has identified potential pathways and barriers for commercial thermal treatment of ASR. Whilst there were many claiming that processing of ASR was possible none have so far shown both the technological capability and economic justification.

High pyrolysis efficiency was maintained throughout the operating/experimental conditions and varying process temperatures. The results of pyrolysis by-products analyses suggest that thermal treatment may represent a viable process for ASR waste and allow the char or syngas to contribute to meeting the EU Directive targets. PST for the reduction of cables and wiring in the raw ASR will need to be employed in order to

achieve the required energy recovery efficiency by the removal of both chlorine and catalytic metals which lead to dioxins and furan production.

The project was funded by the Innovate UK through the Knowledge Transfer Partnership (KTP). The KTP is a UK-wide activity that helps businesses to improve their competitiveness and productivity by making better use of knowledge, technology and skills within Universities, colleges and research organisations.

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Last, but definitely not least, I wish to express my love and gratitude to my whole family for their encouragement and support throughout every step of my career.

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Latin letters

Capital letters

ID	internal diameter
MW_e	megawatt electric
MW_{th}	megawatt thermal
P	pressure (Pa)
T	temperature (^oC)

Small letters

d	day
hr	hour
t	tonne

Greek symbols

ρ	density
θ	angle
μ	dynamic viscosity (cP)
u_f	bulk gas velocity (m/s)

Subscripts

AR	as received
max	maximum
mix	related to mixture
nd	not disclosed
PT	related to Pre-treatment
Vol	volume
Wt	Weight

Abbreviations

ABS	Acrylonitrile Butadiene Styrene
ASR	Automotive Shredder Residue
BFB	Bubbling Fluidised Bed
BS	British Standard
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CAS	Chemical Abstract Service registry number
CFB	Circulating Fluidised Bed
CHP	Combined Heat and Power
CNG	Compressed Natural Gas
COD	Chemical Oxygen Demand
CV	Calorific Value
CVgross	Gross Calorific Value
CVnet	Net Calorific Value
DOC	Dissolved Organic carbon
DRO	Diesel Range Organics
EC	European Commission
ELVs	End-of-Life Vehicles
EPA	US Environmental Protection Agency
EPRS	European Parliamentary Research Service
EU	European Union
FB	Fluidised Bed reactor
FC	Fixed Carbon
FGD	Flue Gas Desulphurisation
FTIR	Fourier Transform Infra-Red
GC	Gas Chromatography
GC-ECD	Gas Chromatography Electron Capture Detector
GC-FID	Gas Chromatography Flame Ionisation Detector
GC-MS	Gas Chromatography Mass Spectrometry
GRO	Gasoline Range Organics
HV	Heating Value

HHV	Higher Heating Value
ICE	Internal Combustion gas Engines
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
IEA	International Energy Agency
IGCC	Integrated Gasification Combined Cycle
KTP	Knowledge Transfer Partnerships
LHV	Lower Heating Value
LOI	Loss on Ignition
LPG	Liquefied Petroleum Gas
MRO	Mineral Oil range Organic
MSW	Municipal Solid Waste
ORC	Organic Rankine Cycles
PA	Poly Amides
PAH	Polycyclic Aromatic Hydrocarbon
PCBs	Polychlorinated Biphenyls
PE	Poly Ethylene
PID	Proportional Integral Derivative controller
PP	Poly Propylene
PS	Poly Styrene
PST	Post Shredder Technologies
PU	Poly Urethane
PVC	Polyvinylchloride
PUF	Polyurethane Foam
QA	Quality Assurance
R&D	Research & Development
RDF	Refuse Derived Fuel
RSD	Relative Standard Deviation
SD	Standard Deviation
SEM-EDX	Scanning Electron Microscopy-Energy Dispersive X-ray
TOCs	Total Organic Carbon
TPHs	Total Petroleum Hydrocarbons
VM	Volatile Matter

WP	Work Programme
XRD	X-ray Diffraction

CHAPTER 1 GENERAL INTRODUCTION, AIMS AND OBJECTIVES

1.1 Introduction and background

In the UK, an average of 1.6 to 2 million vehicles reach the end of their life each year [Gov.UK, Environmental management – guidance]. To recover useful materials, in particular metals (steel and iron, electronics, other non-ferrous metals and aluminium alloys), vehicles are shredded. However, before this occurs a legal requirement is depollution of the vehicle. This is one of the most critical steps in vehicle recycling process and removes: fluids, oil filters, liquefied petroleum gas (LPG) tanks, compressed natural gas (CNG) tanks, catalytic converters, tyres and batteries. Dismantling of vehicles follows, the steps where reusable components parts (e.g. tyres, windscreen and bumpers) may be reused/recycled [Vermeulen et al. 2011]. Finally, the vehicle is shredded.

The ELV is shredded through a fragmentiser and metals are recovered through the use of ferrous and eddy current separators. The materials that remains after these recovery processes is referred to as automotive shredder residue (ASR) [Cossu & Lai, 2015]. ASR contains all the non-metallic residues like glass, fibre, rubber, foam, fluff, grit, paper, wood and a mixture of plastics (mainly made up of four polymers (polyolefins (polyethylene (PE) and polypropylene (PP)), polyvinylchloride (PVC), polyurethane (PU)), polystyrene (PS), two phase polymer blend acrylonitrile butadiene styrene (ABS) and nylon (polyamides, PA)). As a minimum, 50% of the ASR holds valuable recoverable materials. Theoretically, ASR currently comprises around 20-25% of the initial ELV mass. It is anticipated that in the future, as the composition of vehicles changes due to light weighting and new material usage (polymer substitution), the amount of ASR will rise [Davies, 2012; Alonso et al. 2007]. An additional change to vehicles composition is the increase in electronic components units and the resultant presence of high value resources such as gold and rare earth metals [Cucchiella et al. 2016; Restrepo et al. 2017].

The revised ELV directive [EC, 2000] set a target of 95% that required a minimum of 85% of material be recycled or reused, while the additional 10% can be met by processing unrecyclable materials through waste to energy facilities or recovering material like glass for use in aggregates. In addition, the new EU circular economy package [EPRS, 2016] are driving the automotive manufacturing industry towards zero waste to landfill. A total reuse and recover rate of 88.1% ELV was achieved in the UK in 2012 according to European Commission by the Department for business, Innovation & Skills (BIS) [letsrecycle.com].

The UK auto and recycling sectors claimed, in order to meet the demanding new EU target, that came into effect at January 2015 (requiring 95% of ELVs by weight be recycled or recovered), a massive investment by their members would be needed in both new capacity and new technology. These technologies (known as post-shredder technologies (PST)) usually include mechanical separation plants and thermal recovery plants. The mechanical separation plants may or may not be attached directly to the shredder. The technologies used are: (i) magnetic separation for ferrous, (ii) eddy current magnets for non-ferrous, (iii) trommels, (iv) suction for foams and light material and (v) sink-float separation for plastics. Occasionally handpicking stations are employed to achieve the highest level of materials separation. The configuration of the mechanical separation/downstream processes is variable for companies, resulting in a variation on ASR compositions and production from one firm to another. Therefore, for ASR management, it is necessary to understand the ASR production process and to investigate its composition. Within the UK, what is typically left after ASR sorting is landfilled.

Thermal treatment of ASR either by pyrolysis (conversion to liquid), gasification (conversion to gaseous) or combustion (with heat recovery) technologies [Hubble et al. 1978; Zolezzi et al. 2004; Viganò et al. 2010] will reduce the amount of material that requires final disposal. The ASR's non-combustible fraction, which is made up of following: glass, dirt, rock, sand, moisture and residual metals, can be further separated and recycled.

In 2012, the UK government stated that the use of residual materials from ASR as a fuel in designed energy plants. Unfortunately, little evidence for any government proactive support for this to appear. Currently, there are no UK facilities that use ELV waste for energy generation. It has fallen to the metals recycling industry to develop the infrastructure for energy generation from ASR.

Many researchers investigating ASR pyrolysis [e.g. Donaj et al. 2010; Santini et al. 2012; Roh et al. 2013; Haydary et al. 2016; Mayyas et al 2016_a; Mayyas et al. 2016_b; Rey et al. 2016; Notarnicola et al. 2017] have focused on the pyrolytic liquids, gases and chars with varying levels of success. The relative distribution/yield of these products is dependent on the type of feedstock and pyrolysis operating parameters such as: (i) operating temperature, (ii) reactor type, (iii) residence time and (iv) heating rate of the feedstock [Williams, 2005]. Modification of the pyrolysis temperature will yield the following: (i) predominantly char at low temperature ($\leq 450^oC$), (ii) liquids/oil at moderate temperature (450–700^oC) and (iii) predominantly gases at high temperature ($\geq 800^oC$).

Harder & Forton, (2007), Vermeulen et al. (2011) and Cossu et al. (2014), in their comprehensive review concluded that the use of ASR pilot-scale pyrolysis experiments was limited. The majority of testing undertaken was at lab-scale (mg - g hr^{-1}). Galvagno et al. (2001) have produced a detailed ASR pilot-scale trial. In order to apply the ASR pyrolysis at an industrial scale, additional research is required at kg $minute^{-1}$ scale plants. At this scale, the practicalities and challenges associated with the processing of the ASR materials compositions needed to be considered. Ideally, fully commercial plants are required. Currently, there are only three plants or processes that are considered semi or fully commercial proven [Cossu et al. 2014]. These are the Ebara plant (PKA process) in Japan, the Pyromelt process (Lurgi Ensorgung) in Germany and the TWR process (Siemens; Schwel-Brenn; TWR/Mitsui) based in Japan. It should be noted that all three plants are co-processing ASR: for example, the Ebara plant mixes sewage sludge in a 70/30 ratio [Selinger et al. 2003]. From the review of the literature (Chapter 2), there is relatively little information in the open literature about the ASR thermal-processing plants available globally.

Due to both 1) limited information on commercial ASR to energy plant; 2) changing ASR composition and its wide variability, further research is required such as ASR characterisation (produced from a shredder plant), by-products of ASR if subjected to thermal treatment, to identify post ASR management and treatment.

1.2 Aims, Objectives and Scope of Study

Aims

This project aim was to determine optimum chemical and physical properties of automotive shredder residue (ASR) to generate gas through the use of thermal processes.

Objectives

Specific objectives are;

- To characterise ASR produced from a UK shredder plant (as a case study).
- To thermally process ASR using a pilot-scale plant appraise the products generated.
- To optimise thermal process conditions to create gaseous products from thermal treatment of ASR.
- To evaluate available commercial thermal technologies for processing ASR.

Scope of Study

In order to achieve these aims and objectives, the following scope of work was followed:

- Production of ASR: A shredder plant in the Northwest of the UK was used as a case study for ASR characterisation.
- ASR characterisation: Used various physical and chemical analysis techniques including but not limited to bomb calorimeter, Inductively Coupled Plasma

Mass Spectrometer (ICP-MS) and Gas Chromatography high resolution Mass Spectrometry (GC-MS).

- Pilot-scale experiments: ASR thermal processing at a range of conditions using a pilot-scale rotary kiln with a capacity up to 100 kg hr^{-1} feed rate [based at Mitchell Dryers – CAD Works Engineering Ltd, Carlisle, UK].
- Assessment of commercial thermal technologies worldwide with a production capacity (kg hr^{-1}): A review was conducted of the thermal processing plants available globally. The evaluation of the companies and their technology was based on a criteria list created (company experience of the technology, economic consideration, plant environmental impacts are an example of criteria were in the list).

Several parts of this work have already been presented (as oral presentations, posters and papers at conferences) and published in journals (see list of publications in Appendix D).

1.3 Thesis structure

This thesis is divided into five chapters and four appendices and is organised in the following:

CHAPTER 2 presents a review of literature pyrolysis and gasification conversion technologies (in term of process descriptions, operating conditions, components type and products) supported by commercial available technologies worldwide and experience dealing with the waste related to the research area of ASR.

CHAPTER 3 details the experimental set-up methodology and analytical techniques employed in this study. Preliminary study of commercial assessment of the conversion technologies were presented.

CHAPTER 4 presents the commercial assessment outstanding issues and understanding, experimental results and discussions on the results obtained from the ASR pyrolysis in a pilot-scale plant.

CHAPTER 5 lists the conclusions and suggestions for further study.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

In order to meet the challenges of dealing with ASR on a commercial scale a general overview was required on the range of pyrolysis or gasification thermal conversion technologies to deal with ASR. The many pyrolysis reactor technologies developed around the world for bio-oil, bio-char, syngas productions and/or energy, power-related applications were assessed for the potential application of ASR. A similar approach was taken for gasification technologies. This was underpinned by research studies on ASR even though their commericalisation had yet be realised.

2.2 Pyrolysis conversion technologies

2.2.1 Pyrolysis process

Pyrolysis of waste/biomass produces liquid (bio-oil), solid and gaseous fractions in the absence of oxygen or air. Depending on the operating conditions, the technique types are conventional (slow), flash and fast pyrolysis [Maschio et al. 1992]. Table 2.1 presents the typical operating parameters for pyrolysis process. Conventional pyrolysis can produce solid, liquid and gaseous under a slow heating rate range from 0.1-1°C/sec at an operating temperature of 300-700°C. Flash pyrolysis occurs under a faster heating rate (≥ 1000°C/sec) and produces liquid in significant proportions. Similar to the flash technique, fast pyrolysis is heating the waste/biomass to a temperature of 450-550°C but with a lower heating rate of 10-200°C/sec with no air to vaporise by rapid cooling.

The products obtained from pyrolysis of waste/biomass are oil (vapours that at ambient temperature condense to a dark brown viscous liquid), char and gas. Relative distribution of products is dependent on pyrolysis type and pyrolysis operating parameters as shown in Table 2.2.

Table 2.1 Typical operating parameters for pyrolysis process

	C pyrolysis	**Fast pyrolysis**	**Flash pyrolysis**
Operating Temperature (°C)	300 - 700	450 - 550	800 - 1000
Heating rate (°C/s)	0.1 - 1	10 - 200	≥ 1000
Solid residence time (s)	600-6000	0.5 - 5	< 0.5
Particle size (mm)	5 - 50	< 1	Dust < 0.2

Table 2.2 Typical products for pyrolysis process

Pyrolysis	**Product yield (%)**		
Process	**Oil**	**Char**	**Gas**
Slow	30	35	35
Fast	50	20	30
Flash	75	12	13

Source: [Balat et al. 2009; Bridgwater, 2007]

2.2.2 Pyrolysis reactor types

The heart of pyrolysis process is the reactor and has been the topic of significant research, innovation and development. This has been to improve the essential characteristics of: high heating rates, moderate temperatures and short vapour product residence times for pyrolysis products. Originally, pyrolysis reactor developers had assumed that small waste/biomass particles size (less than 1 mm) and very short residence time would achieve high bio-oil yield, however later research found different results that particle size and vapour residence time have little effect on bio-oil yield, whereas those parameters greatly affect bio-oil composition [Wang, 2006; Wang et al. 2005]. A number of reactor designs were explored to optimise the pyrolysis performance; however, each reactor type has specific characteristics, bio-oil yielding capacity, advantages and limitations. A comprehensive study on description, advantages and disadvantages of different types of pyrolysis reactors presented in Table 2.3. Whereas, schematics diagrams of some described reactor types are shown in Figure 2.1.

Only about 25 years ago, the pyrolysis technology development started when the benefit of liquefying waste/biomass were gradually recognised, although laboratory studies have been carried out for much longer. Throughout late 1980s and early 1990s, the main area of the research and development were special reactors like Vortex reactor [Diebold & Scahill, 1988; Diebold & Scahill, 1997], rotating blades reactor [Peacocke, 1994], rotating cone reactor [Wagenaar et al. 1995; Prins & Wagenaar, 1997], cyclone reactor [Lede, 1986], transported bed reactor [Rossi & Graham, 1997], vacuum reactor [Roy et al. 1988] and the fluid bed reactor [Rossi & Graham, 1997; Scott & Piskorz, 1982].

Then from late 1990s the process development arisen worldwide causing to construct many pilot plants, for example in Spain (Union Fenosa), Italy (Enel), UK (Wellman), Canada (Pyrovac, Dynamotive), Finland (Fortum) and Netherlands (BTG) as well as many small/lab and pilot scale pyrolysis bio-oil plants established and operated by different research organisations. Some of these are listed in Table 2.4. The aims of the companies to use bio-oil for energy production in addition to chemicals. Many pilot-plant projects have stopped after initial testing (e.g. the plants of Union Fenosa, Enel, Wellman, Fortum, and Pyrovac's large-scale installation in Jonquiere, Canada). This may have related to legislative limitations, economic prospects and markets.

Research concluded that none of the rector concepts completely satisfies all requirements in their existing development. However, it was noted that capital intensive, simple process, using the smallest possible gas to waste/biomass feed ratio. These; operated efficiently on a small scale and were scalable. Therefore, proved to be the most useful. Table 2.5 explains the valuation of the different reactor technologies, given these considerations.

It is evident that fluidised bed reactors (BFB & CFB) are currently the most popular reactor as well as commercially available in producing bio-oil from biomass through pyrolysis technology followed by auger, ablative, rotating cone and vacuum reactors. Microwave and plasma looks promising technology because of its easy to scale up.

Table 2.3 Description, advantages & disadvantages of different Pyrolysis reactors

Reactor	Description	Advantages	Disadvantages
BFB	Heated sand is used which rapidly heats the feedstock in none oxygen environment where it is decompose into char, vapour & aerosols. Fludising gas stream carries decomposed constituents out of the reactor. Char removed by a cyclone separator & stored. Remaining vapour rapidly cooled with quenching system, condensed into bio-oil & stored.	High quality bio-oil yield. Char does not accumulate in the fludised bed, but it is promptly separated. Residence time of solids & vapour is controlled by fludising flow rate.	To achieve high feedstocks heating rate, material particle sizes (< 2-3 mm) required.
CFB	Similar features to BFB except shorter residence times for chars & vapours. This effects in higher gas velocity & char content in bio-oil than in BFB.	Suitable for very large throughputs, even though hydrodynamics are more complex.	Char is finer.
Plasma	Made with a cylindrical quartz tube surrounded by two copper electrodes. Feedstock are fed at the middle of the tube using screw positioned on the top of the tube. Electrodes are coupled with electrical power to produce thermal energy to gas flows through the tube. Oxygen is removed by an inert gas & also aids as working gas to produce plasma. Vapours products removed from reactor by vacuum pump.	Tar formation is eliminated. High energy density & temperature produced which provides a possible solution for problems occur in slow pyrolysis like generation heavy tarry compounds & low productivity of syngas.	High electrical power consumption.
PyRos	Applied in a cyclonic reactor with combined hot gas filter in one unit to produce particle free bio-oil. Feedstock & inert heat carrier are introduced as a particles into cyclone & solids are transported by recycled vapours from process. By centrifugal force the particles are moved downwards to periphery of cyclone. During the transport downwards, feedstock particles are dried, heated up & devolatilised.	Short gas residence time (0.5 – 1 s) means secondary cracking reactions of tars can be reduced. Average process temperature is 450-550°C.	Alkali dissolved in the oil. Solids in the oil.
Rotating cone	Pyrolysis reaction takes place upon mechanical mixing of feedstock & hot sand, instead of using inert gas. Feedstock & sand are introduced at the base of the cone while spinning causes centrifugal force to move solids upwards to the lip of the cone. Vapours directed to condenser while char and sand sent to combustor.	Less wear. High bio-oil yield.	The design is complex.
Entrained Flow	Inert gas introduced & combustion in the reactor bottom section. Hot flue gas flows upwards through the tube while passing feedstock to heat materials particles.	Shorter residence times (0.2 s) can reduce tar yield.	Increase in pressure will affect the temperature profile within the reactor (changing operating condition).

Table 2.3 Description, advantages & disadvantages of Pyrolysis reactors *Cont.*

Reactor	Description	Advantages	Disadvantages
Microwave	Feedstock carried out in a microwave cavity oven powered by electricity. Inert gas is flowing continuously (create O_2 free atmosphere & to serve as carrier gas).	Unexpected formation of hot spots which increases syngas yield. High efficiency heat transfer. Uniform temperature supply.	High electrical power consumption.
Ablative (Rotating disk, Vortex)	Mechanical pressure is used to press feedstock against heated reactor wall. Particles in contact with wall melts & as it moved away, residual oil become vapours. In Rotating Disk reactor, feedstock forced to slide on a hot rotation disk become soften & vaporise. In Vortex reactor, feedstocks are entrained in hot inert gas (steam or N_2) flow & then enter the tube at high velocity make particles melted & leave a liquid film of bio-oil. Vapours generated swept out by carrier gas in 50-100 ms.	Feedstock does not require excessive grinding. No inert gas medium required in rotation disk.	Low reaction rate.
Auger	Augers are used to move feedstock through an O_2 free cylindrical heated tube causes devolatilise & gasify (char, gases condensed as bio-oil, non-condensable vapour as bio-gas)	Compact. Lower process temperature.	Moving parts in hot zone.
Vacuum	Perform on a slow pyrolysis process. Moving metal belt conveys feedstock (periodically stirred by mechanical agitator) into high temperature vacuum chamber. A burner & induction heater are used with molten salts as a heat carrier to heat the feedstock.	Produce clean oil.	Lower bio-oil yield. Slow process. Generates more water.
Ceramic ball downflow	Mainly made of steel tube. During the pyrolysis, feedstock & ceramic balls (heat carrier) were fed into the reactor & pyrolysed vapours were discharged to the quench system to produce bio-oil under slightly negative pressure environment.	High solid-liquid conversion rate. Energy self-sufficient. Easy operation.	Utility features (e.g. increase in corrosion temperature, in oxidation & erosion resistance)
Moving bed & Fixed bed	Typical fixed bed reactor made of firebricks, steel or concrete with a fuel feeding unit, an ash removal & gas exit. Feedstock move down a vertical shaft & contact upward moving product gas stream. In moving bed reactor, feedstocks are continuously introduced at the top & the fluid flow together down the reactor.	Reliable. Simple design.	Difficult to remove tar. Operate with high carbon conversation. Long solid residence time (i.e. flow of solids not easy to maintain).

Source: [Bridgwater, 2012; Lam et al. 2010; Menedez et al. 2004; Ringer et al. 2006; Scott et al. 1999, Gupta et al. 2014]

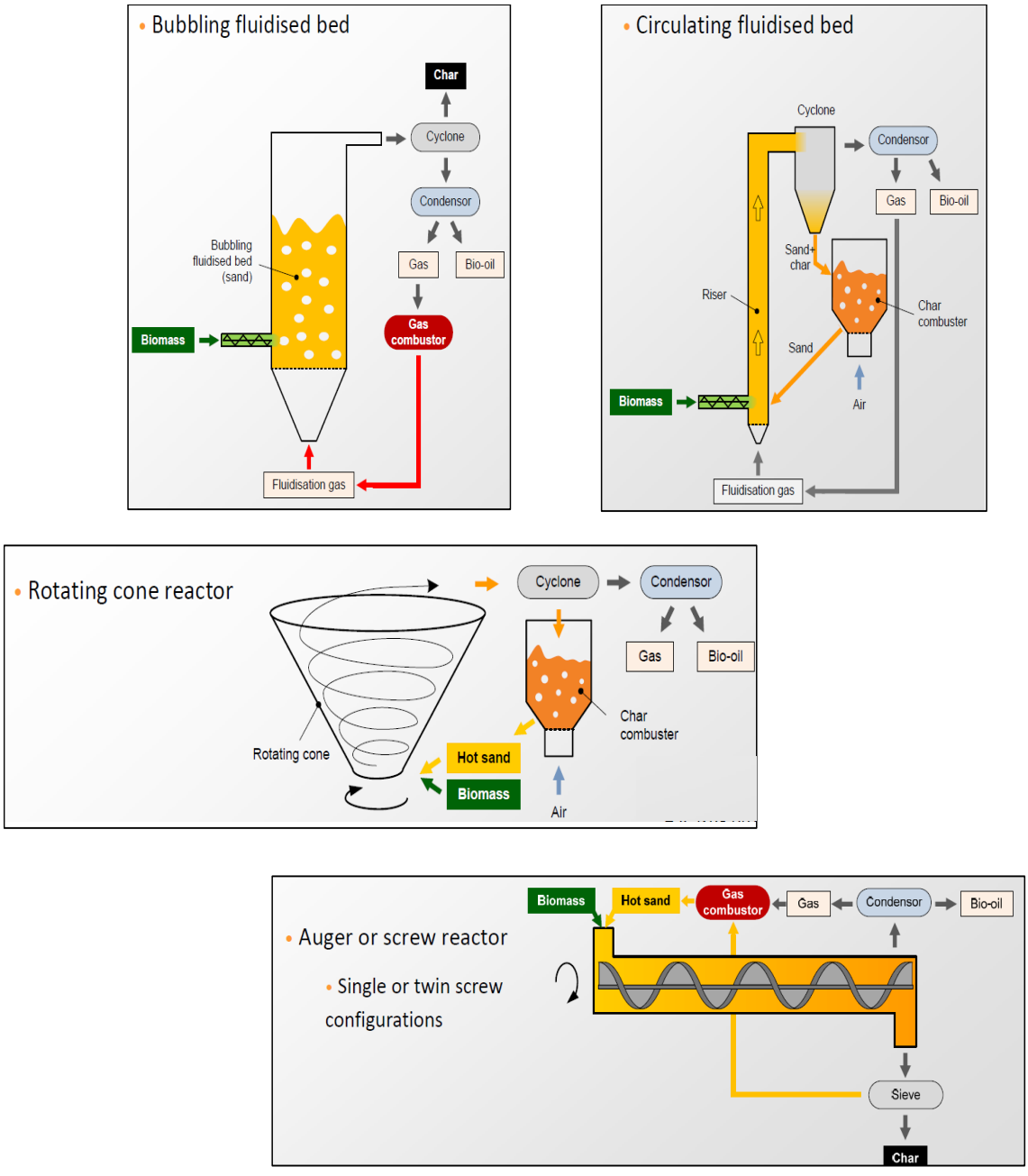


Figure 2.1 Schematic diagrams of some pyrolysis reactor types.
Source: [Ronsse et al. 2013]

Table 2.4 Worldwide pyrolysis reactors

Reactor	Plant owner/country	Feedstock	Capacity kg hr^{-1}
BFB	Dynamotive/Canada	Agriculture	8000
	Wellman/UK	Wood chips	250-500
	Biomass Eng Ltd/UK	Biomass	200
	Agritherm/Canada	Sawdust, oil seed, bagsse	200
	RTI/Canada	Biomass (wood)	20
	TNO/Netherlands	Biomass	10
	Guangzhough Ins/China	Biomass	10
	NREL/USA	Biomass	10
	Texas A&M Uni., USA	Biomass, MSW	42
	Campinas Uni./Brazil	Biomass (manure), forest	100
	Science & Tec. Uni./China	agricultural waste residues	650
	Alten/Italy	Wood & Agri.	500
	Union Fenosa/Spain	Wheat straw, pine, wood	150
	Waterloo Uni./Canada	Agriculture	2
	Daekung ESCO, Ltd/ Korea	Oil palm EFB, pine, kelp	1-2 t d^{-1}
	EBRI, Aston Uni/UK	Biomass, algae	200
	Fortum/Finland	Wood, forest residue	10000
	Warwick University/UK	Plastics, willow, sewage sludge	5-25
CFB	Dynamotive/Canada	Agriculture	400
	Ensyn/USA-Canada	Biomass (wheat straw)	1000
	ENEA/Italy	Oilseeds, RDF	650
	ENEA/Italy	Biomass	100
	Metso-UPM/Finland	Wood, sawdust, forest res.	400
	GRES/Greece	Wood	10
	VTT/Finland	Biomass (forest residue)	20
Plasma	FCIPT/India	Medical waste	20
PyRos	TNO/Netherlands	Modelling/Biomass	30
Rotating cone	BTG/Netherlands	Palm (EFB)	2000
Entrained flow	Egemin/Belgium	Wood	200
	Ensyn/USA-Canada	Food (liquid smoke)	1000
Entrained fluid	GTRI/USA	Wood	50
Microwave	Minnesota Uni./USA	Algae, straw, MSW, wood	10
	Cambridge University/UK	Tyres, automotive oils, vegetable oils	0.4-5
	York University/UK	Wheat straw, wood	30
Ablative mill	Aston Uni./UK	Wood, biomass	20
	BBC/Canada	Tyre	50
	Thermophysics Ins of Eng./Ukraine	Biomass, MSW	15
Rotating disk	PYTEC Thermo. Anlagen GmbH/Germany	Wood, pine wood, wheat straw	250
Vortex	Solar energy research/USA	Biomass	30
Auger	Renewable Oil Int./USA	Biomass (various)	200
	FZK/Germany	Straw	500
	Texas A&M Uni., USA	Biomass, MSW	30
	Abritech/Canada	Agriculture	2083
	Lurgi LR/Germany	Biomass	500
Integral catalytic	TNO/Netherlands	Biomass	30
	UCL (Uni)/UK	Plastic waste	1-5
Vacuum	Pyrovac/Canada	Biomass (softwood bark)	50
Cer. ball downflow	Shandong Uni of Tec./China	Biomass (rice straw)	110
Moving bed & fixed bed	Edinburgh University/UK	Rise husk, wheat straw, miscanthus, OSR, softwood	1-50
	Sheffield University	Waste wood, textile residues	1
	Cranfield University	Biomass	18
	Anhui Yineng Bio-energy Ltd/China	Biomass, sewage sludge	600
	Bio-alternative/Switzerland	By-product oil	50

Source: [Boulard, 2002; Bridgwater, 2012; Brown, 1996; Jahirul et al. 2012; PYTEC, 2005; Ringer et al. 2006]

Table 2.5 Comparison of various reactors (considering selection criteria)

Reactor	Complexity	Status	Size	Inert gas need	Feed Size	Scale up
BFB	Medium	Commercial	Medium	High	Small (< 3 mm)	Easy
CFB	High	Commercial	Medium	High	Large	Medium
Plasma	High	Commercial	Unknown	Low	Small	Easy
PyRos	Low	Pilot	Low	Low	Unknown	Hard
Rotating cone	High	Commercial	Low	Not required	Small	Medium
Entrained Flow	High	Demonstration	Medium	High	Small	Easy
Entrained Fluid	High	Pilot	Medium	Unknown	Unknown	Unknown
Microwave	Low	Pilot	Unknown	Low	Large	Easy
Ablative (Rotating disk, Vortex)	High	Pilot	Low	Low	Large (≤ 20 mm)	Hard
Auger	Medium	Demonstration	Low	Not required	Medium	Medium
Integral Catalytic	High	Commercial	Unknown	Unknown	Unknown	Unknown
Vacuum	High	Demonstration	High	Not Required	Large (2-5 cm)	Hard
Ceramic ball downflow	Low	Pilot	Medium	Unknown	Unknown	Easy
Moving bed & Fixed bed	High	Commercial	Medium	High	Small	Easy
Commercial: 2 – 20 t hr^{-1}		Demo.: 200-2000 kg hr^{-1}		Pilot: 20-200 kg hr^{-1}		Lab: 1-20 kg hr^{-1}
Complexity: mechanically/requires high investment and maintenance costs						

Favorable Feature: Commercial, Low, Large & Easy, Moderate Feature: Demonstration, Pilot & Medium, Unfavorable Feature: Lab, High, small & Hard, Unknown=i.e. not reported): Source: [PYNE IEA Bioenergy http://www.pyne.co.uk]

2.2.3 Pyrolysis products

Bio-oil (mainly derived from cellulose component of waste/biomass), bio-char (came from the lignin component of waste/biomass), syngas (originated from the hemicellulose component of waste/biomass), are the three primary products from pyrolysis technology. Table 2.6 presents a brief description and various applications used for each pyrolysis products. Whereas, Table 2.7 illustrate the issue that relate to the price of the pyrolysis products.

Table 2.6 Pyrolysis products description & applications

Products	Description	Applications
Bio-oil from Pyrolysis	Bio-oil is a dark brown complex homogeneous mix of water (20-25%wt) & oxygenated compounds (~ 300-400, 45-50% O_2) such as carbonyls, carboxys, phenolics with an advantages of CO_2 balance, high-energy density compared to waste feedstock & transportability. During storage, the bio-oil becomes more viscous because of chemical & physical changes (as volatiles lost & many reactions continue) but the effects can be reduced if it stored in cool place. Low temperature pyrolysis technology with high heating rate and short gas residence time can led to high yield. Bio-oil viscosity (μ) range 35-1000 cP (at room temperature), therefore require mild heating to pump easily.	**Heat (**Co-firing of boiler & furnace**. Power (**diesel engine & turbine). **Chemicals** (Resins**,** fertiliser**,** flavors**,** adhesive**,** acetic aside**,** industrial feedstock)**. Fuels** (Hydrogen**,** upgrading).
Bio-Char from Pyrolysis	Bio-char consists mainly of carbon along with hydrogen & various inorganic species in two structures (stacked crystalline sheet & amorphous aromatic). Bio-char is defined as the solid carbon rich product with chemical & physical characteristics (e.g. particle size, moisture content, pH) vary widely depending on the converted feedstock. Also, reactor type & pyrolysis operating conditions effects the char physical characteristics. For example, higher heating rate operating conditions, shorter residence time & finer feedstock produce finer bio-char whereas slow pyrolysis with larger particle size feedstock produce coarser bio-char.	**Agricultural** (include soil amendment **(**to improve soil health), greenhouse growth media, fertiliser & carbon sequestration). **Activated carbon** (bio-adsorbents can be created from bio-char & use in land reclamation, water remediation or air emission control through adsorption of heavy metals, pollutants/contaminants). **Heat source** (bio-coal can be created via torrefaction (mild pyrolysis 200-300^{o}C) for heat & power generation). **Other** (include metallurgical & advanced materials manufacturing (e.g. nanotubes, fibers) under development).
Syngas from Pyrolysis	Syngas consist mainly from H_2, CO & small amount of CO_2, H_2O, N_2, hydrocarbons (such as CH_4, C_2H_4, C_2H_6), tar & ash. H_2 is produced from the cracking of hydrocarbons whereas CO & CO_2 formed from the presence of oxygen in the feedstock. Therefore, the amount of cellulose present in the feedstock (as a highly oxygenated polymer) is an important factor predicting the amount of CO_2 produced. Syngas yield is hugely influenced by the pyrolysis reactor temperature (e.g. Tang & Huang, 2005 produced up to 76.4% syngas in plasma pyrolysis reactor). Molar ratio of H_2 & CO in syngas in an important factor that governs its possible applications (e.g. higher H_2/CO molar ratio is desirable to produce Fisher-Tropsch synthesis for transportation fuel production & to produce hydrogen for ammonia synthesis [Fernandez & Menedez, 2011])	Can be a renewable alternative fuel for internal combustion engines & industrial combustion processes. Commercial petrol & diesel engines can be easily modified to use for power generation & transportation.

Table 2.7 Pricing of pyrolysis products

Products	Issue that relates to pyrolysis products pricing
Bio-oil from Pyrolysis	• Market for bio-oil is still developing • Currently not traded commodity, however combustion bio-oil in CHP is the most probable commercial use • Close value of bio-oil can be measured in comparison its heating value to heavy fuel oil. • Other close value based on the price of electricity generated & the cost of the local fuel source (e.g. natural gas). In Canada, the price of electricity from biomass reported $0.13/kW. • The cost of the fuel source to the boiler burner tips & system efficiency must be considered.
Bio-Char from Pyrolysis	• Market available • Bio-char has a value comparable to the relative heat content of the heating media displaced from the heating system. Can compete with all fossil fuel. • Bio-char with sufficient quality form can be pricey. • Raw bio-char & bio-char blended with other materials are being sold in many countries. Average price reported $2.48 per kilogram
Syngas from Pyrolysis	• Raw syngas should be cleaned & conditioned in order to meet the specification of catalytic synthesis processes such as Fischer-Tropsch diesel & methanol. • Technologies most often will include filters, rectisol unit (acid gas removal), gas polishing (e.g. by ZnO & active carbon filter), water gas shift reactor & CO_2 removal unit. • The world market for syngas is dominated by the ammonia industry followed by production of hydrogen for use in refineries. • Syngas (produced by processing municipal solid waste in a plant with one reactor) priced of $100-300 per $1/m^3$ reported by Syntes Engineering, Denmark.

Source: [IBI, 2013; Marshall, 2013; Van der Drift & Boerrigter, 2006]

Researchers in recent time are paying more attention on maximising the overall oil yield from pyrolysis processes rather than paying sufficient attention to the product quality and upgrading of bio-oil. Table 2.8 presents a reported maximised bio-oil yield and typical heating method for different types of the pyrolysis reactors. Heat transfer in pyrolysis reactors is one of the main concerns; however, several heating methods are used in different pyrolysis reactors to ensure the efficient conversion of waste/biomass

into liquid fuel. Thermal conductivity of waste/biomass is too low, therefore given the reliance of the waste/biomass particle on gas-solid heat transfer, the size needs to be reasonable for rapid heating in order to achieve high bio-oil.

Poor volatility, high viscosity, moisture content and corrosiveness of bio-oil limited to use commercially. However, more homogenous bio-oil liquid (if generated from processing lower molecular weight compounds rather than high molecular weight derived compounds (come from lignin present in the waste/biomass)) can be used to generate heat and power. Table 2.9 shows the comparison of fuel properties and composition between standard diesel oil and pyrolysis bio-oil for plastic and tyre feedstocks. Some of the complications of using bio-oil as a fuel in standard equipment such as boilers, engines and gas turbines are listed in Table 2.10.

Table 2.8 Bio-oil yield & typical heating methods used of pyrolysis reactors

Reactor	Bio-oil yield	Heating method
BFB	70 – 75%	Heated recycle gas
CFB	70 – 75%	Wall & sand heating
Plasma	30 – 40%	Radio frequency
PyRos	70 – 75%	PyRos heating
Rotating cone	65%	Gasification of char to heat sand
Entrained Flow	Unknown	Unknown
Microwave	60 – 70%	Electromagnetic
Ablative (Rotating disk, Vortex)	70%	Wall heating
Auger	30-50%	Fire tube
Vacuum	35-50%	Direct contract with hot surface
Ceramic ball downflow Moving bed & Fixed bed	35-50%	Furnace or kilns

Source: [Jahirul et al. 2012; Tang & Huang, 2005; Fidalgo et al. 2008; Zhao et al. 2010]

Table 2.9 Properties of pyrolysis oil (plastic & tyre) to diesel oil

Property	Tyre pyrolysis oil	Plastic pyrolysis oil	Diesel oil
HV (kJ kg^{-1})	43225.9	461990.12	45814.74
C (%)	84.67	83.79	87
H (%)	10.44	11.36	13
O (%)	4.17	2	-
Cl (%)	N/A	0.03	N/A
S (%)	≤ 1	-	-
Density *(ρ)* at 30°C (g/cm^3)	0.924	0.8147	0.7994
Viscosity *(μ)* at 40°C (cP)	2.69	2.49	1 – 4.11
Flash Point (°C)	68	100	70

Source: [Wongkhorsub & Chindaprasert, 2013]

Table 2.10 Summary of bio-oil application in boilers, turbines & diesel engine

Application	Issue that relates to use bio-oil
Furnaces & Boilers	• Because of furnaces & boiler are commonly used for heat/power generation & operate with variety of fuels, bio-oil can be suitable to use as long as it meets acceptable emission levels & consistent quality characteristics. • Can replace heavy fuel oil. • Different bio-oil qualities differ in combustion behaviour & exhaust gas emissions. • Flame from bio-oil combustion is longer compared to fossil fuel. • Modification of the burners may require.
Diesel Engines	• Bio-oil may utilize in medium & slow speed diesel engines. • Blends of bio-oil & methanol can be use in high speed engines. • Carbon deposition on pistons & composition chamber components, filter plugging, injector coking, heavy gum & wax formation, engine wear, poor atomisation, fuel pump failure of lubricating oil, high CO emissions were reported. • Use of better materials for engine components to overcome of these problems.
Gas Turbines	• Gas turbines are operated using liquid & gaseous petroleum fuels for power generation, industrial production processes & providing power for aircraft. • Carbon deposition in the combustion chamber, slag build-up in the exhaust system, high CO & HC emissions were reported. • Modify & redesign can efficiently burn bio-oil.

2.2.4 Cost of pyrolysis plant

Pyrolysis plants main components are the reactor which represents about 10%-15% of the total capital cost whereas other costs of waste/biomass handling (e.g. grinding, storage) and pyrolysis products collection. Pyrolysis plant cost can be classified into two main categories; capital investment and operating cost as shown in Figure 2.2.

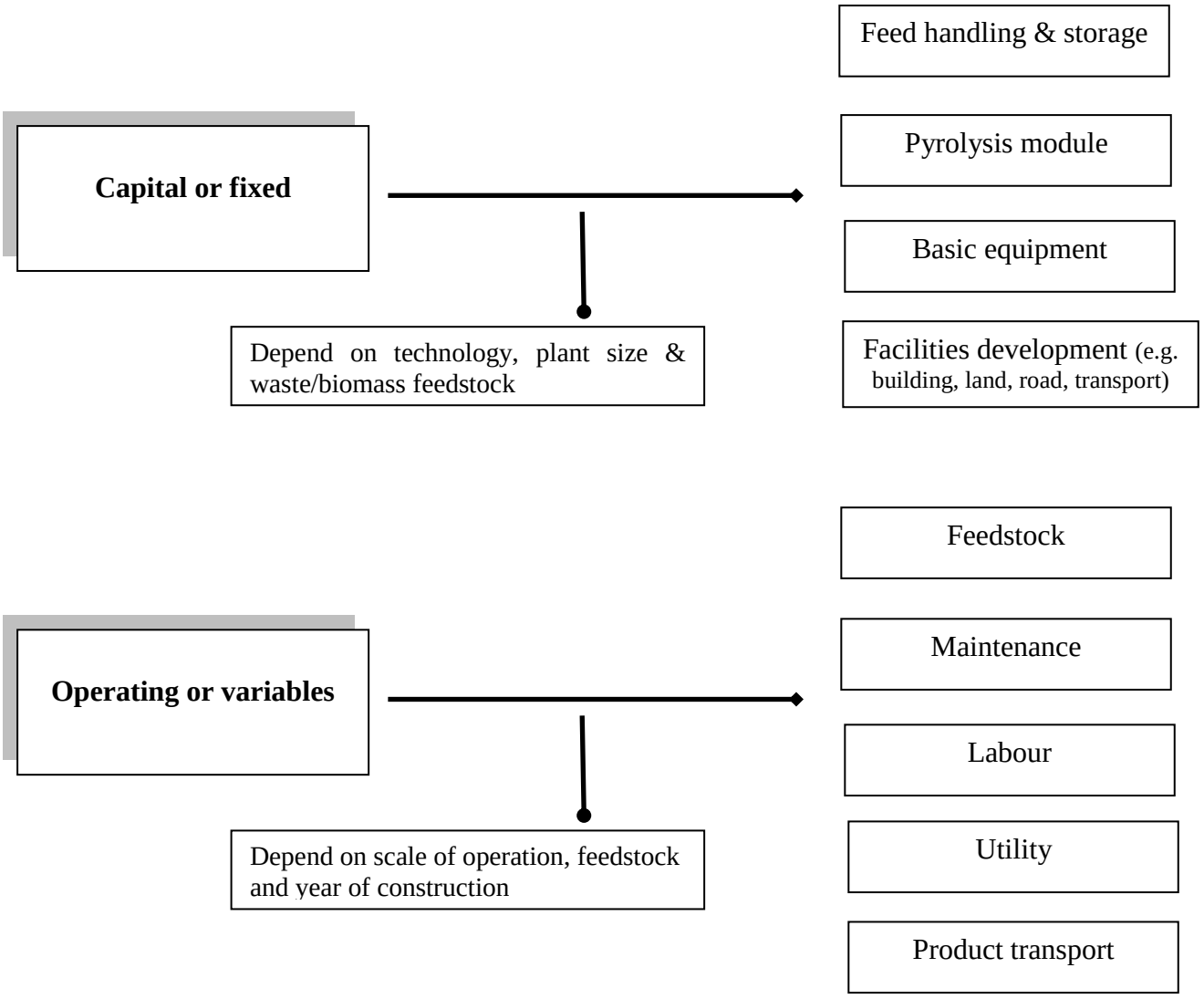


Figure 2.2 Cost of pyrolysis plant categories

The plant cost is the summation cost of the main base equipment, which can be determined via published data and quotes from the manufactures. To obtain total plant cost, the base equipment cost is usually multiplied by different factors like direct-cost factor, building factor, site improvement factor and utilities factor. Annual production cost can be determined by the following [Islam & Ani, 2000; Polagye, 2007; Thews & Kuppens, 2008; Voets & Kuppens, 2011]:

Annual cost ($) = Operating cost + (annualised capital cost – annualised salvage value)

Eq. 2.1

Equations 2 & 3 can calculate annualised capital cost and construction cost respectively;

$$ACC = \frac{(total\ plant \cos t + construction \cos t)}{\{1 - (1 + i) - Np\}} \times ip$$

Eq. 2.2

$$Construction\ cost = \sum_{j=1}^{Nc} \frac{Total\ plant\ cost}{Nc} Jic(1 + ip)^{Nc-J+1}$$

Eq. 2.3

Where,

ACC = annualised capital cost per year

i_p = is the interest rate,

N_p = is the plant life time,

N_c = is the construction period,

i_c = is the construction financing/interest rate,

i_p = is the project financing rate.

Several studies reported pyrolysis plant cost (includes; plant size, feedstock type, capital investment, annual operating cost & estimated pyrolysis bio-oil product cost) are summarised in Table 2.11.

Table 2.11 Summary of reported pyrolysis plant cost

	Plant Size ($t\ d^{-1}$)	Feedstock	Capital investment (M $)	Annual operating costs (M $)	Feed costs ($/t)	Production costs ($/gal)
2017	2000	Forest residues	427	154	69	6.25
2015	2205	Woody biomass	546	25.41	80	3.46
2013	2205	Woody biomass	700	37.66	80	3.39
2010	2000	Corn stover	200	12.3	83	0.26
2007	1650	Wood pellet	180	12	-	0.24
1994	1000	Dry wood	68	10.6	44	0.41
1994	1000	Wet wood	72	11.3	30	0.60
2003	1000	Peat	76	10.2	20	0.61
2003	1000	Straw	82	10.2	42.5	0.64
2004	900	Wet wood	46	9.9	34	0.50
2006	550	Dry wood	48.2	9.6	45	0.71
2002	400	Wet wood	14.3	8.8	36	1.02
1992	250	Dry wood	14	8.92	44	0.55
2002	200	Wet wood	8.8	4.84	36	1.11
2002	100	Wet wood	6.6	2.84	36	1.48
2000	24	Rice husk	3.89	0.170	22	0.82
2000	2.4	Rice husk	0.97	0.34	22	1.73

Source: [Carrasco et al. 2017; Dutta et al. 2015; Jones et al. 2013; Ringer et al. 2006; Solantausta & Oasmaa, 2003; Mullaney et al. 2002; Islam & Ani, 2000; Polagye et al. 2007; Wright et al. 2010; Luo et al. 2004; Gregoire, 1992; Gregoire, 1994; Cottam & Bridgwater, 1994]

2.3 Gasification conversion technologies

2.3.1 Gasification process

Waste/biomass can be converted by gasification into a gaseous fuel mixture in the presence of limited amounts of oxygen or air. There are different types of gasification technology options operating in various conditions (e.g. temperature range from 800-900°C for fludised bed gasifier reactors or ≥ 1200°C, for entrained flow reactors/systems). The gas mixture produced (syngas) consists mainly of CO, H_2, CH_4,

CO_2 and N_2. This can be used for chemical production such as methanol or as a fuel gas input into engines or turbines to generate power [Palz & Chartier, 1980]. The syngas needs to be cooled and passed through a cleaning train system to remove impurities such as tar and alkali metals. Feedstock pre-treatment (PT) is an essential issue prior to feeding into a gasifier reactor. For example, drying may use to decrease the moisture content whereas milling can be necessary in order to transform the feedstock into a more uniform material (which in turn leads to an increase in particle surface area facilitating inter-particle bonding). Gasification with air is cheaper option than gasification with oxygen. However, oxygen gasification provides a better quality syngas with a heating value of 10-18 MJ/Nm^3 compared to syngas from air gasification of 4-6 MJ/Nm^3 and containing up to 60% N_2.

2.3.2 Gasification reactor types

A number of reactor designs have been developed for gasification process like fixed bed gasifier (updraft and downdraft), fluidised bed gasifier (bubbling (BFB), circulating (CFB)), entrained flow and indirect gasifier. Fluidised bed gasifier is a bed of fine solids where silica sand transformed into a liquid state by interaction with an upward flowing gas. Usually operates at a lower temperature (~ 700-900^oC) with heat transfer efficiency five times higher compared to a fixed bed gasifier [Belgiorno et al. 2003]. Rotary kiln gasification systems use similar kiln commonly found for example in cement and lime industries. Each reactor type has specific characteristics, syngas quality, advantages and limitations. A comprehensive study on description, advantages and disadvantages of different types of gasification reactors presented in Table 2.12. Other reactors such as cyclonic or vortex, doubled fired, molten bath, plasma arc have not covered here because of either of tiny literature knowledge available, currently under development and/or hard to scale up/operate commercially (e.g. plasma arc gasification is not commercially proven to treat MSW). Schematics diagrams of the described reactor types shown in Figure 2.3.

Table 2.12 Description, advantages & disadvantages of different gasification reactors

Reactor	Description	Advantages	Disadvantages
BFB	Air or O_2 introduced at the bottom of the bed (sand, limestone, dolomite or alumina) acting as a fluidising oxidant medium. Bed commonly designed with a larger cross section area to obtain desired gas-phase residence time for complete devolatilisation. The bed preheated to the fuel ignition temperature (in waste/biomass ~ 540^{o}C) using hot flue gas. Then, a slowly feed introduce into the bed to raise the bed temperature (T) to operating range ~ 790-847^{o}C. BFB density (ρ) & gas (u_f) velocity are about 720 kg/m^3 & 1.5-3.7 m/s, respectively.	Good gas-solid mixing & high heat transfer, causing uniform bed conditions. Carbon conversion can reach 95-99%. Low tar content (typically < 1-3 mg/Nm^3) in syngas. Easy startup & shutdown. Proven technology in power industry.	Limitation of scale (typically employed for small to medium scale applications). PT feeding processing essential (usually fuel size < 2 inches). Carbon may loss with bed ash. Extensive air pollution control required. High operational & maintenance costs.
CFB	Gas flow is larger than BFB resulting gas bubbles become higher, forming great voids in the bed/collected & entraining significant amounts of solids. Turbulent bed solids are separated from the gas flow & return through a solid circulation loop. CFB density (ρ) & gas velocity (u_f) are about 560 kg/m^3 & 9.1 m/s, respectively.	Similar features to BFB.	Similar features to BFB except the scale limitation issue.
SFB	Spout-fluidised bed where high velocity gasifying agent injected through single inlet (orifice or spout) at the centre bottom part of the bed. This generate high velocity region bed centre & fountain on bed surface.	This cyclic pattern proved to using coarse particles. Recently, attracted to converting MSW & various biomass to syngas.	High circulation rate of particles may result to non-uniform distribution operating conditions.
Downdraft	Fuel is fed from the top & gasifying agent (air or O_2) is fed either from the top or sides of the gasifier & flows downwards through the reactor in the same direction (co-current). Four stages taken place during gasification process; 1) drying zone (occurs at the top of the reactor at temperature of ~ 100^{o}C) where waste/biomass heated up & getting dried; 2) devolatilisation or pyrolysis zone (at T ~ 400^{o}C) where tars, vapours & char mostly created; 3) combustion zone (at T of ≥ 900-1200^{o}C) where devolatilisation products burns to form hot gases (containing CO_2 & H_2O), char & ash; 4) reduction or gasification zone (occurs at the bottom of the reactor at T of ~ 900^{o}C) where gases reacts & reduced to form CO & H_2.	Syngas contains low tar (tar conversion ≥ 99%). Produce low ash. High solids residence time. Simple design /construction. Short time require to start up.	Exit syngas T ~ 700^{o}C resulting low system efficiency. Dry (low moisture content ≤ 20%) uniform sized (< 2 inches) feed fuel require. Limitation of scale.

Updraft	Fuel is fed from the top & gasifying agent (air or O_2) is fed from the bottom of the gasifier & flows upwards through the reactor (counter-current). Similar features to downdraft four stages gasification process except that the combustion zone occurs at the bottom of the reactor at T of ≥ 900-1200^{o}C where char burns to form CO_2 & H_2O to flows upwards to the down flowing solid into the reduction zone to form CO & H_2. Then, the flow gases in their direction contacted to the dry waste/biomass at the devolatilisation zone to form char followed by drying zone where gases/vapours dried further preforming exit syngas temperature ~ 80-100^{o}C.	Higher overall efficiency due to low syngas temperature leaving the gasifier. Flexible to fuel feed size & high moisture content fuel composition (~ 50%). Easy to scale up.	Syngas contains high tar & oil which initially produced at devolatilisation/ pyrolysis zone. CO & H_2 in syngas reported lower. Long time may require to start up.
Entrained Flow	Fuel with gasifying agent can be flow in the gasifier downwards, upwards or horizontal. Entrainment is a region where air-filled transports achieved when gasifying agent flow velocity increased high putting force on the solid particles to exceeds their weights. Occur at high oxidation T ~ 1300-1400^{o}C which means that ash removed as a liquid slag.	Syngas free of tar & has low CH_4 content. High fuel conversion.	High cost of feed preparation (due to reduce moisture content & particle size to its low levels requirement). Safety concern as operation at pressure. Slagging of ash. Refractory life concern for waste/biomass feeds.
Rotary Kiln	Fuel is fed in the upper end of a slowly rotating kiln (refractory lined steel cylinder) with controlled air/O_2 mix. Tumbling action causes mixing gasifying agent with fuel at high T (~ 1000-1400^{o}C) for gasification process to occur. Syngas usually captured within the kiln & directed from the high side of the kiln. Key element design; 1) end seals (to minimise air leakage & prevent combustion gases escape), 2) drive assembly (to supply enough torque to rotate the kiln under all operating conditions), 3) kiln refractory (refractory lining (tile) to protect the kiln shell from overheating and/or chemical attack), 4) control system (includes surfaces near feeding system & discharge area/ash removal must designed for resistance to high impact/thermal shock loads & withstand chemical attack/slag penetration, respectively).	Fuel type & particle size not dependent, therefore, has the ability to use a variety of fuel type/size over time (with no modifications). Low operational & maintenance costs. Low emission. Kiln rotation speed varies in the range of ¾ to 4 revolutions per min.	Limited ability to control air for robust gasification reported. Few manufactures with experience.

Source: [Bain, 2004; McKendry, 2002; Basu, 2010; Quaak et al. 1999; Vinayak et al. 2013]

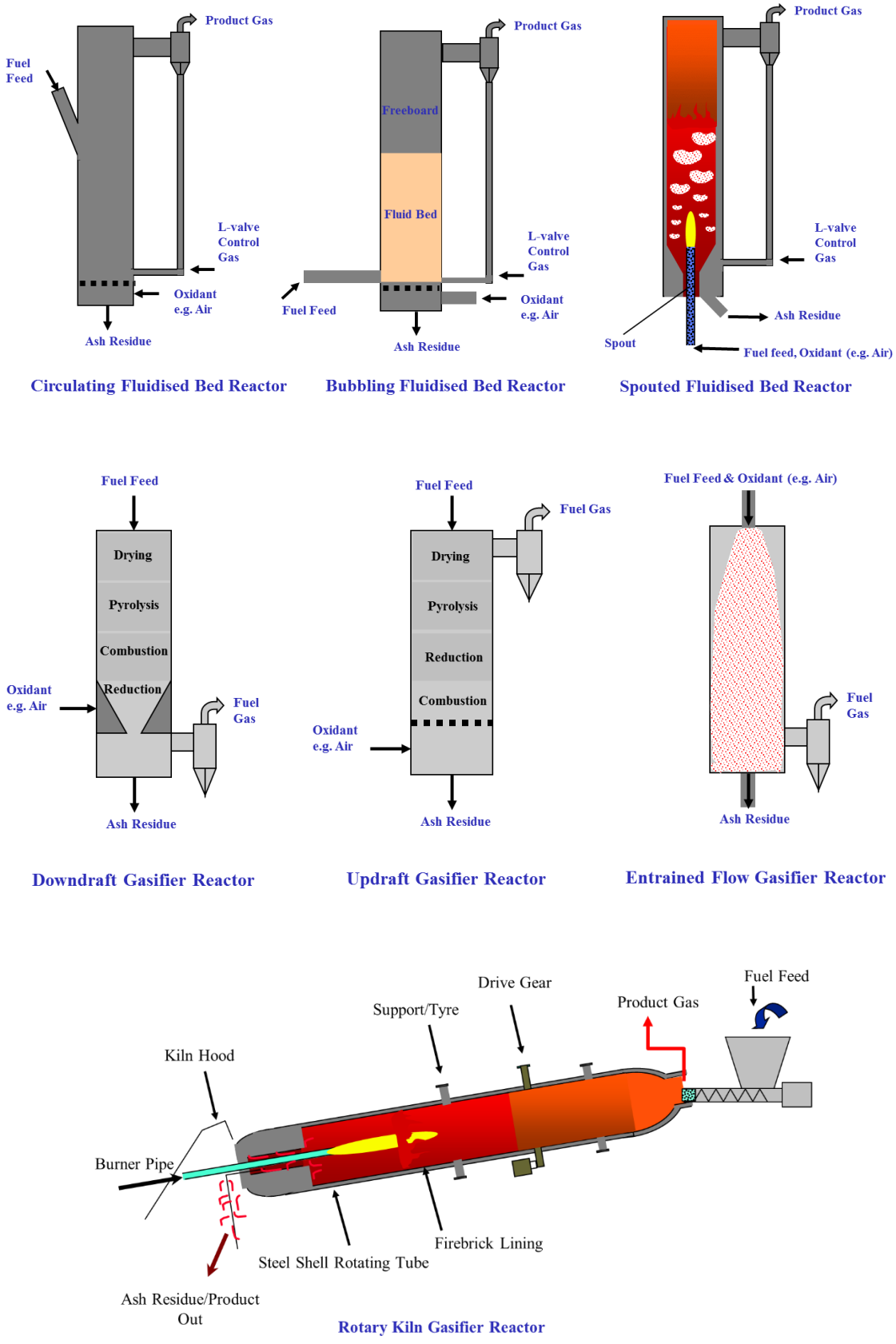


Figure 2.3 Schematic diagrams of gasifier reactor types

2.3.3 Gasification process parameter and reactors effects

Parameters of pressure, temperature, residence time, heating rate, mode of gas/solid contact, moisture content and particle size range reported a great influence on gasification process reactions and products distribution. Table 2.13 summarise the valuation of the different reactor technologies, given these considerations.

Table 2.13 Comparison of various reactors considering gasification process parameters

Parameters	BFB	CFB	SFB	Downdraft	Updraft	Entrained Flow	Rotary Kiln
Operating Pressure (P)	1-35 bar	Similar features to BFB	High	> 20 bar	> 20 bar	1-85 bar	Almost run at negative pressure
Operating Temperature	800-1100^{o}C	Similar features to BFB	800-1100^{o}C	> 1000^{o}C	> 1000^{o}C	> 1200^{o}C	> 1200^{o}C
Temperature gradient	Very Uniform over entire FB	Similar features to BFB	Uniform over cross section of the bed	Not uniform on the middle section	Not uniform on lower section	Significant temperature both axially & radially	If air leaking in will cause temperature drop along
Oxidant demand	Moderate	Similar features to BFB	Moderate	Low	Low	High	Not reported for waste feedstock
Gas/solid contact	Complex flow motion. Low gas velocity, inert solid stays in	Complex flow motion. Inert solid elutriated, separated & re-circulated	Gas outward from spout & solid systematic circulation patterns	Solid & gas moves down	Solid down & gas up	No inert solid, has high gas velocity & can be run as cyclonic reactor	Gives good gas-solid contact
Residence time	Short residence time	Similar features to BFB	Short residence time	Long residence time but shorter than updraft	Long residence time	Seconds to several seconds. Short residence time	Long residence time (> 7 min RDF reported)
Feedstock moisture content	10-55%	5 – 60%	~ 50%	~ 50%	≤ 20%	~ 15%	Not important
Particle size	< 50-150 mm	< 20 mm	~ 1-3 mm	< 50 mm	< 50 mm	< 1mm	Not important

Source: [Moulijn et al. 2001; McKendry, 2002; Epstein & Grace, 2011; Basu, 2010; Molino et al. 2013; Janajreh & Adeyemi 2014; Mahinpey & Gomez, 2016]

2.3.4 Gasification products and environmental concerns

Syngas is the main product of gasification process. However, the quality of syngas depends on some factors like the reactor type, feedstock, processing conditions (e.g. temp., pressure, oxidant used). Table 2.14 presents the typical syngas purity & syngas contaminants influenced by different gasification reactor technologies, whereas, Table 2.15 shows a brief discussion of the nature of the key contaminants presented in syngas.

Table 2.14 Typical syngas temperature & syngas contamination of various reactors

Parameters	BFB	CFB	SFB	Downdraft	Updraft	Entrained flow	Rotary kiln
Syngas Temperature	900-1050ºC	Similar features to BFB	N/A	400-700ºC	80-100ºC	1250-1600^{0}C	850-950ºC
Syngas purity	Moderate-high (tar & particulate)	Similar features to BFB	N/A	Low (tar, dust, oils & phenols)	Low (tar, dust, oils, phenols)	High (almost tar free but with soot)	Very high (even higher in indirect rotary kiln)
Tars (g/Nm^3)	1 - 15	Similar features to BFB	N/A	0.1 – 1.2	20 - 100	Low (< 0.1)	0.000038
Particulate (g/Nm^3)	2 - 20	Similar features to BFB	N/A	0.1 – 0.2	0.1 – 1.0	Low (< 0.2)	Not reported for waste feedstock
Alkali compounds (ppm)	Depend on the feedstock (e.g. scrap tires; Na: 200-600, K: 200-600). Alkali salts mixt with low melting points may cause defluidisation.	Similar features to BFB	Similar features to BFB	Depend on the feedstock (e.g. RDF; Na: 3000-5000, K: 2000-3000). Cause alkali slagging on surfaces of fly ash	Similar features to Down-draft	Similar features to Down-draft	Depend on the feedstock (e.g. wood saw dust; Na: 40, K: 500). May cause operating problems
Nitrogen-containing compounds	NH_3 & HCN high formation (NH_3 can react with Cl forming NH_4Cl causing corrosion)	Similar Also, may form amines (very hard to remove from syngas)	Similar features to BFB	Low NH_3 & HCN formation – (due to higher residence time operation)	Similar features to Down-draft	Moderate NH_3 & HCN formation (to short RT but high temp. operation)	Low NH_3 & HCN formation – (due to high residence time operation)
Sulphur	Depend on feedstock	Similar	Similar	Similar	≤ 20%	~ 15%	Not important

Source: [Graham & Bain, 1993; Neeft et al. 1999; NREL, 2001; Higman et al. 2003; Paterson et al. 2005; Shi et al. 2016]

Table 2.15 Syngas contaminants & typical removal (cleaning-up system)

Contaminants	Description	Removal
Tars	Is a complex range of oxygenated aromatic organic compounds where the composition is highly dependent on the gasification temperature & residence time reaction condition in the reactor. As syngas cools downstream of the reactor, such materials condense in the gas stream as vaporised or as aerosols or small liquid droplets (tar formation) which may lead to blockages in in pipework. At low temperature (~ 450^{o}C) tar composition can be primary oxygenated whereas mixture become more complicated to high molecular weight/deoxygenated products (like ethers (phenolic, alkyl, heterocyclic), polyromantic hydrocarbons (PAH)) at high temperature (~ 950^{o}C). For example, Tars formed at moderate temperatures in updraft reactor are composed of oxygenates & phenolic ethers where tars formed at high temperature in CFB reactor contain heterocyclic ethers & PAHs.	• Wet scrubbers • ESP (electrostatic precipitators) • Catalytic tar destruction
Particulate	Typically, are the solid-phase materials contain the inorganic (ash) driven from the mineral matter in the feedstock. It presented in a form of coarse particulates to fine fly ash. Other source of particulates is the char (occurs when feedstock gasified incomplete). Particulates can damage downstream equipment; therefore a control system is essential particularly in large- scale gasifier system.	• Cyclone filters • Barrier filters (ceramic candle, bag & packed filters) • Wet scrubbers • ESP
Alkali Compounds	Particularly K & Na (determined from the chemical composition of the ash with the mineral matter) above ~ 800^{o}C (typical operating temperature in gasification system) can vapours/condense to small particulates (< 5 μm (fine solids)) or aerosols which may deposition on cooler downstream surfaces & may be corrosive to metal surfaces.	• Cyclone filters • Ceramic filters & packed filters employing activated bauxite
Nitrogen-containing compounds	To avoid NOx emissions (when syngas burned) is necessary to remove Ammonia (NH_3) from the syngas. NH_3 acceptable levels dictated by local regulations. Generally, NO_x not present in high enough concentrations in gasification system.	• Wet scrubbers • Catalytic destruction
Sulphur	Sulphur in feedstock may converted to sulphur oxides (SO_x), carbonyl sulphide (COS) formation hydrogen sulphide (H_2S) into SO_2 in the gas downstream causing corrosion.	• Wet scrubbers • FGD (Flue-gas desulphurisation) • Limestone injection • Claus process

Source: [Baker et al. 1986; Baker, 1998; Evans & Milne, 1997; NREL, 2001]

Table 2.16 presents an overview of the syngas contaminants with the potential problems that can arise, whereas Table 2.17 shows the type of alkalis/trace metals required to be aware and/or analyse as may great concern of environment and/or gasification system.

Table 2.16 Syngas contaminants & its potential problems

Contaminant	Example	Issue of concerns
Tars	Refractory aromatics	Clogging of filters
Particulates	Ash, char, fludised bed materials	Erosion
Nitrogen compounds	NH_3, HCN	Emission
Sulphur, Chlorine	H_2S and HCl	Corrosion, emissions, catalyst poisoning

Table 2.17 Effects of the Alkalis/Trace Metals on gasification system & environment

Alkalis/Trace Metals	Issue of concerns
Na/K	Superheater/engine corrosion, catalyst poisoning
As, B, Cd, Hg, Mo, Pb, Se	Greatest environmental concern
Cr, Cu, Ni, V, Zn	Moderate environmental concern
Ba, Co, Ge, Li, Mn, Sb, Sr	Minor environmental concern
Be, Sn, Te, TI	Low concentration elements of concerns
Rn, Th, U	Radioactive elements

2.4 Syngas for electricity generation (power systems)

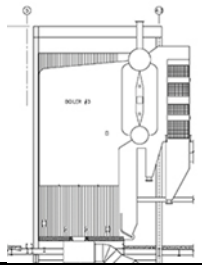
Syngas for power generation can be use one of the following systems:

- Turbine
- Engine
- Boiler

- Combined cycle (which combine a gas turbine & steam turbine, (CHP))
- Fuel cell

Table 2.18 presents a brief description includes operation, advantages and disadvantages of different types of power systems. The level of contaminants removal from the syngas plays a major role to choose between these applications. Table 2.19 summarises desirable syngas characteristics for engine and boiler applications. In combined heat and power (CHP) plants the product gas of waste/biomass usually fired on gas engine without problems if have calorific values of about 5-6 MJ/m^3 [Boerrigter & Rauch, 2006]. Boiler application usually, related to injecting the syngas in the combustion zone of existing coal power plants. Researchers reported that co-firing percentage up to 10% are achievable without the need for modifications of the coal boiler. In addition, if the producer gas is not cleaned then it can only be used as fuel for a boiler that provides steam for a turbine or for providing heat only. With contaminants, internal combustion gas engines (ICE) are more tolerant than gas turbines. For example, Milne et al. (1998) reported that it is possible to have tar content up to 50-100 mg/Nm^3 for ICE and less than 5 mg/Nm^3 for gas turbines. Hasler & Nussbaumer, (1999) tabulated (see Table 2.20) the typical values of the particulate and tar contents requirements in the syngas (after cleanup) for power generation using IC engine and gas turbine. In the IC engine applications, the gas should not only be cleaned, but also cooled to increase is volumetric efficiency. It should be noted to the fact that gas engines and gas turbines are more efficient than steam turbines (combined cycle). The electrical efficiencies of a small turbines range between 20-25%, where the highest sizes reached near to 40%. Gas engines or gas turbines can be directly or indirectly in contact to gasifier/pyrolysis unit capable of firing the syngas produced. The direct technology may know as Integrated Gasification Combined Cycle (IGCC).

Table 2.18 Power generation systems

Type	Turbine	Engine	Boiler	Combined cycle	Fuel cell
					
Description	Consist of three main sections: compressor, combustor & turbine.	Normally are reciprocating piston engines.	Is a devise/firebox with various sizes to create steam.	Made of combustion engine & heat recovery generator.	Consist of anode, cathode & electrolyte in a cell.
Operation	Operates on the principle of the Brayton cycle where compressed air is mixed with fuel & burned under constant pressure conditions. The resulting hot gas is expanded through a turbine to perform work.	Operation concept is: intake (fuel injection), compression, combustion (by spark), expansion & discharge (hot gases release). The cycle regularly repeated.	Fuel is fed into boiler/furnace operated under high temperature in order to burn the fuel & generate heat where transferred to water to make steam.	Heat can be recovered both from hot flue gases that leave the engine & from cooling water (cylinder jackets at T ~ 90^{o}C). Latter a low temperature/pressure (~ 200^{o}C, some bars) steam will produce.	Fuel (normally H_2) feed to the node (negative electrode) while air is being supplied to cathode (positive) allows chemical reaction takes place by means of an ions exchange & produce power.
Advantages	• High power output (range 50 kWe – 240 MW_e) • It can be designed for a small size & weight • Rapid installation • High operation speed • Fuel flexibility • Low pollutant emissions • Zero water consumption for cooling • Low operating pressure	• High power output (100 kWe – 1 GWe) • High reliability • Fuel flexibility • Low cost (800-1200 €/kWe) • Low pressure injection of gas • High efficiency (50 – 60%) • High service life (60,000 - 80,000 hr) • High flexibility (operation)	• High power output (22 kW – 22.5 GW) • High syngas cleaning may not require • Reliability • Known technologies • Safety • Affordability • Easy operation • Can obtain various temperature	• High power output (10 kW – 400 MW) • Fuel flexibility • Low emissions • Low noise & vibrations • Low maintenance • High service life (40,000 - 60,000 hr) • Self-sustaining feature • High efficiency (45 – 50%)	• High power output (range 10 kWe – 100 MW_e) • Operate silently • No emissions. Only water • No energy to operate • Low heat transmission • Low maintenance • High efficiency (60 – 80%)
disadvantages	• High cost • Low efficiency compared to ICE • Efficiency (range 18 – 40%) • High operating temperature • Longer startup compared to ICE	• Emissions (NOx, CO) • Considerable noise & vibration • Heavy weight • Cooling required	• Low boiler efficiency of waste co-firing • Emissions • High maintenance • Corrosion • Ash formation • Fuel feed control	• Small-scale high cost (2500 - 3000 €/kW) • Low electrical efficiency • Startup time is significant • Waste application still at early stage	• High cost (3000 €/kWe) • High syngas cleaning required • Long operation time • Technology under development (e.g. electrolyte type).

Source: [Macchi et al. 2006; Sawyer, 1985; Pulkrabek, 1997; LM2500; DPS]

Table 2.19 Desirable syngas characteristics for electricity application

Fuel gas/Syngas	Boiler	Turbine
H_2/CO	Unimportant	Unimportant
HV	High (efficiency improves as heating values increases)	High (efficiency improves as heating values increases)
P (bar)	Low	5-20
T (^oC)	250	500-600
Hydrocarbons	High	High
CO_2	Not critical	Not critical
N_2	N_2 lowers the heating value, but level is unimportant as long as syngas can be burned with a stable flame	Similar features to boiler
H_2O	Low	Can tolerate relatively high water levels (sometimes steam added to moderate combustion temperature to control NOx)
Contaminants (e.g. dust, volatile metals)	Small amount of contaminates can be tolerated	Low particulates/metals

Source: [U.S DoE, 2002]

Table 2.20 Gas quality requirement/syngas conditioning for power generation.

Contaminant	IC engine	Gas turbine
Particles (mg/Nm^3)	< 50	< 30
Particle size (µm)	< 10	< 5
Tar (mg/Nm^3)	< 100	N/A
Alkali metals (mg/Nm^3)	N/A	0.24

Source: [Hasler & Nussbaumer, 1999]

In theory, the use of fuel cells (burns H_2) for power is an attractive alternative for the use of gas engines because of the potential higher electrical efficiencies. However, fuel

cell is in principal a catalytic process required a much stricter gas specifications as following:

- Sulphur must be completely removed (as it is a poison to the fuel cell).
- Tars, aliphatic and aromatic hydrocarbons must not be high (quantitative specification are not yet research reported).
- Nitrogen-free gas is not required.
- H_2 level of concentration in syngas may ~ 99.9%.

There are other technologies (e.g. Stirling engines) that could be potentially used for power generation from syngas. They have not been considered in this study because of either immaturity of the technology or small scale. However, Organic Rankine Cycles (ORC) deserve a brief description. Commercial solutions of ORC are normally available in the power capacity range of 200 kW_e – 2.5 MW_e. The technology is based on a closed Rankine cycle, where the working medium is organic fluid suitable when the feeding (e.g. syngas, heat) at temperature of ~ 70 – 400^oC. The working fluids must have several features such as low flammability, low freezing point, low toxicity, low cost and high density [Quoilin, 2007]. The latter evaporates from the working fluids flows through a turbine, yielding mechanical power that is converted to electric by means of the alternator. Therefore, this option usually used in waste heat recovery (e.g. from exhaust gases exiting internal combustion engines, industrial furnaces) rather than hot valuable syngas produced in the gasification or combustion systems. A typical electrical efficiency of a waste/biomass fired ORC system is about 15%, but the recovery of the condensation heat allows to reach a very high thermal efficiency, about 75% [Obernberger et al. 2002]. This is why the CHP configuration is normally preferred.

2.5 ASR pyrolysis and gasification studies

Previous studies reported the gasification [De Filippis et al. 2003; Cho et al. 2010; Lin et al. 2010; Viganò et al. 2010; Donaj et al. 2011; Mancini et al. 2014] and pyrolysis [Braslaw et al. 1991; Shen et al. 1995; Day et al. 1996; Rausa et al. 1997; Chaala et al.

1999; Day et al. 1999; Galvagno et al. 2001; Roy & Chaala, 2001; De Marco et al. 2002; Chiarioni et al. 2003; Pasel & Wanzi, 2003; Zolezzi et al. 2004; De Marco et al. 2007; Harder & Forton, 2007; Joung et al. 2007_a; Donaj et al. 2010; Donaj et al. 2011; Santini et al. 2012; Roh et al. 2013; Haydary et al. 2016; Mayyas et al. 2016_a; Mayyas et al. 2016_b; Rey et al. 2016; Notarnicola et al. 2017; Anzano et al. 2017; Khodier et al. 2017] as the main processes to recover energy from ASR. Table 2.21 provides a brief overview of some selected ASR gasification and pyrolysis studies.

Most of these studies based on lab-scale trials (mg-g hr^{-1}). Vermeulen et al. (2011), Harder & Forton, (2007) and Cossu et al. (2014) in their comprehensive review concluded that the use of ASR pilot-scale pyrolysis experiments is very limited. In addition, many studies focused on the ASR pyrolysis or gasification processes and product yields. Whereas, the emissions of the processes and the characterisation of the thermal products (in particular char) received less attention. Day et al. (1996) have studied the products from the ASR pyrolysis using a commercial screw kiln unit with a continuous feeding of 200 kg hr^{-1} and corresponded to a residence time of 15 min. The chemical composition of the gas, liquid and solid fractions produced from ASR pyrolysis at 500^{o}C recorded temperature were determined. Results showed that the energy content of the gas product was high and pyrolysis oil contained measurable quantities of sulphur, nitrogen and chlorine containing compounds, which could prevent its direct use as a fuel in many applications. In respect to the residual solids products, the char was discharged from the reactor into a catch pot fitted with a screen separator in order to produce it into two streams: a fines portion and a coarse portion. The particle size distribution, weight loss analysis, heavy metal concentrations and leachability tests were performed on both char portions. Elemental analysis was performed only on the fines fraction and the results highlighted high concentration of carbon, iron, silica, aluminium, calcium and chlorine. They concluded, although heavy metals concentrations were relatively high content of zinc, lead and copper on both fines and coarse char fractions, it does not cause any problems regarding their leachability. Galvagno et al. (2001) have produced a detailed ASR pyrolysis product from a pilot-scale rotary kiln operating under different load (5-7 kg hr^{-1}), residence time capacity up to 40 min and varying process temperatures (550, 600, 680^{o}C). The results showed that

the yield of char increases as the temperature decreases. However, the production of char was favoured over oil and syngas at all studied temperatures. Char concentrations were 59, 44, 43%wt compared to oil of 19, 33, 20%wt and gas of 4, 9, 13%wt at pyrolysis temperature of 550, 600, 680^{o}C, respectively. Leaching tests conducted on char at different temperatures that even both ash and heavy metals content nearly double than that of the original material, the effects on environment is quite similar. Khodier et al. (2017) have investigated the characteristics of the solid fractions (char-fine and char-coarse) produced from a pilot-scale rotary kiln at 800-1000^{o}C with a feeding rate of 10 kg hr^{-1}. The results revealed that the calorific value of the by-product chars in fine fraction were high in every pyrolysis temperature and it is maximal at 800^{o}C. Char-coarse calorific value was low with high ash contents, iron, silica, aluminium, calcium and nickel. They concluded that the segregation of char would assist in optimisation of energy and resource recovery. However, they recommended the necessary to assess the organic pollutant such as PAHs in the char-products obtained at various temperatures. Anzano et al. (2017) indicated that no studies have investigated the distribution of PAHs in the solid residue produced from ASR pyrolysis. In their lab-scale pyrolysis of the ASR, the solid residue produced at 500^{o}C did not detect PAHs, whereas the maximum total concentration of 19.41 ng g^{-1} was observed at 700^{o}C.

Table 2.21 Selected gasification & pyrolysis studies

System Description	Fuel Type	Experiments/ studies	Results	Issues	Remarks	Ref.
Full-scale plant employing a rotary kiln operated for 40 hr between 850-1120°C, with an average feed of 2.4 t hr^{-1}. System was completed with a steam boiler (at 43 bar, 430°C).	Test involved three different materials – 100% ASR and ASR with different percentage of shredding and white goods.	Gasification and Incineration. Characterisation of both ASR feed materials and combustion residues were investigated.	Slag represented ~ 18%wt of the feed could be landfilled hazardous waste, while both fly and bottom ashes of ~ 2%wt had to be classified as hazardous wastes.	Modification of the ASR feeding device was necessary, Also, introduction of a cyclone to reduce flue gas dust was considered.	A pre-treatment for the reduction of fines in the ASR was recommended in order to achieve the required energy recovery efficiency.	Mancini et al. [2014]
Fluidised bed gasifier operated at 590°C followed by a cyclonic afterburner of 1400°C.	ASR	Modelling & LCA analysis of a sequential gasification & combustion processes.	Despite the unfavourable characteristics of ASR, the proposed technology can reach appealing energy performances.	Operation of the afterburner at 1400°C moreover produces a vitrified and hence inert slag.	Since most of the carbon in ASR comes from fossil sources, the CO_2 emissions at the stack are mainly non-renewable.	Viganò et al. [2010]
Lab-scale unstirred stainless steel autoclave carried in fed batch mode at 400, 500 & 700°C in nitrogen atmosphere.	Heavy ASR & light ASR (typical run 100g)	Raw samples & pyrolysis products (solid, liquid, gas) characterised.	Pyrolysis appears to be an appropriate tec. For recycling heavy ASR, since valuable solid (39%), liquid (20-29%), gas (31-41%).	Light ASR does not yield valuable products. 500°C was considered adequate to produce total decomposition of the ASR.	Increasing temperature over 500°C determines gaseous components are increased against liquid products.	De Marco et al. [2007]
Lab-scale conventional pyrolysis/tubular reactor fast pyrolysis carried in fed batch mode at 500, 600, 700, 800°C.	ASR	Compared performance & product yields in conventional pyrolysis & fast pyrolysis.	Carbon conversion in both cases was higher than 80% for temperature ranging from 500-800°C. Conventional pyrolysis maximised gas production (~ 35% coupled with 20% of oil production), while the fast pyrolysis gave an oil yield higher than 55%.	The carbon content of the conventional pyrolysis gas reached 36.4% of the feed at 800°C, while > 69% of the initial carbon was found the pyrolysis oil obtained by the fast pyrolysis at 800°C.	Conventional & fast pyrolysis processes offer an attractive technical solution for ASR energy recovery because of the reduced environmental impact like air pollutions & opportunity of material recovery from chars or tar.	Zolezzi et al. [2004]

2.6 Concluding remarks

It is clear from the literature reviewed above that the by-products produced from gasification or pyrolysis thermal technologies are vary significantly as they can be influenced by technology reactors, process conditions and fuel properties. Another major focus of R&D activities is on solving problems concerning ASR recycling to ensure that energy recovery are realistic alternatives for landfill. Available data about these critical issues are still limited for various ASR by-products. Therefore, it is necessary to thoroughly investigate ASR as feed material and by-products of syngas, oil, char and/or emissions data from gasification or pyrolysis technologies. Also, the use of ASR pilot-scale pyrolysis experiments (as suggested by Vermeulen et al. (2011) and Cossu et al. (2014)), improve designs can be achieved.

Pyrolysis plant cost, reactor types, pyrolysis products, syngas cleaning and power generation systems data were mostly done for fossil fuel or biomass knowledge. It was reported that plant size/capacity of 100 t d^{-1} of wet wood costs a capital investment of $6.6 M with annual operating cost of $2.8 M. For pricing of pyrolysis products, bio-oil market is still developing whereas, bio-char and syngas markets are more advanced. Rotary kiln reactor looks promising in dealing with more complicated feedstock, easy to scale up and can be used for pyrolysis or gasification technologies.

2.7 Summary

The literature review has covered the 4 objectives to the research project. The types of ASR produced and its treatment were reviewed both in terms of processing and meeting legislation targets. There has been detailed evaluation of different available technological solutions in terms of outputs, suitability for ASR and cost.

CHAPTER 3 METHODOLOGY

3.1 Introduction

This chapter presents an outline of the methods and means used to carry out the commercial assessment of the worldwide available pyrolysis or gasification technologies (which includes identification procedures) and the experimental set-up work (which includes the work programme, material of ASR production, materials shredding techniques, sample procedures, pilot-scale plant description and operating conditions, as well as methods of analysis of raw ASR and by-product of syngas emissions and solid residue (char)) for ASR pyrolysis.

Details presented here for both commercial assessment and experimental activities show that the methodology employed was well controlled. The methods were statistically controlled using both process and instrument quality control samples. Both were sourced independently from the solutions used to calibrate the method. Instrument and process blank solutions were also run at regular intervals (with each batch) to monitor potential sources of contamination.

3.2 Commercial assessment of the pyrolysis and gasification technologies

3.2.1 Procedure

A review was conducted of the thermal-processing plants available globally. Initially, all companies were included which had the potential to provide either biomass or waste thermal plants. These companies were subsequently evaluated to determine their potential suitability for use as an ASR thermal process technology provider. Initial screening of more than one hundred identified companies was carried out. This focused on the maturity of their process and its suitability to utilise ASR. From this screening of the technology providers, 79 were selected and contacted in order to collect up-to-date information on the following: (i) services, (ii) products, (iii) technical and (iv) commercial maturity. The evaluation of these companies and their technology was

based on the criteria listed in Table 3.1. The six criteria have defined based on questions raised from UK shredder plant (case study) on which they will select the process to deal with ASR for a further feasibility studies and basic engineering. These criteria were: (i) in random order (as the relative importance has not yet been defined) and (ii) general (as the same questions were sent to all companies).

Table 3.1 List of criteria for shortlisting companies

Criteria	Specifications, description & conditions
Waste type	• ASR
Purpose	• Pyrolysis and/or gasification process to convert ASR to an oil or gaseous fuel, which will be converted to electrical power
Technology provider	• Supplier business nature (i.e. small to large corporation) • Supplier capability such as warranties, potential of OEM (original equipment manufacturer)
Technology plant / Equipment	• Experience of technology (e.g. number of units sold, units in operation) • Materials pre-treatment (e.g. driers cost, screens) • Reliability & availability of the process
Economic consideration	• Capital cost (supply & installation) • Operational costs (£/MW_e output) including maintenance • Technical risk
Environmental impact	• This includes emissions, quantities of residues, plant footprint and stack

3.3 Experimental pilot-scale pyrolysis rig

3.3.1 Work programme (WP)

This research work consists of several groups of work programme associated with ASR characterisations and ASR pyrolysis trials: (WP1) ASR characterisations/analysis (in terms of daily productions, materials compositions, proximate, ultimate, metals and contaminates/toxic (in respect to waste acceptance criteria (WAC)); (WP2) ASR shredding/feeding (materials were crushed prior characterisation and pyrolysis trials); (WP3) ASR pyrolysis using pilot-scale rig; (WP4) Pyrolysis by-products analysis using various analytical techniques. The following diagram (Figure 3.1) is the summary of the ASR analysis and pyrolysis experiments performed:

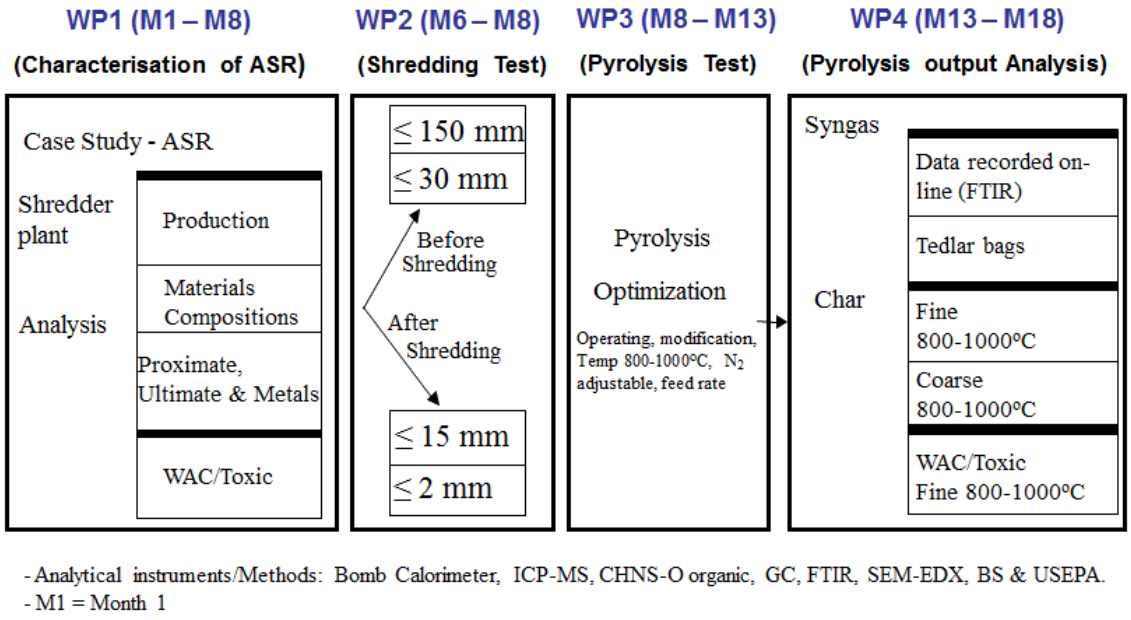


Figure 3.1 Diagram of work programme (WP1-WP4) ASR pyrolysis treatment studies

3.3.2 Sample preparation

3.3.2.1 Production of ASR

A shredder plant in the Northwest of the UK was used as a case study for ASR characterisation. The plant has a capacity of 416 kt per year. The layout of the shredder plant is shown in Figure 3.2. The plant consisted of: (1) a pre-shredder (where ELVs are processed after been depolluted); (2,3), conveyor system; (4), hammer mill; (5), magnetic drums (to separate ferrous and nonferrous materials); (6), quality material control of Z-box and cyclone system (where any remaining ferrous materials will be sent/removed through a Z-box section and any light fraction materials will be sent through the air cyclone separator), followed by (7) a conveyor system where shredded steels filtered and stored ready for export). The ASR is sized, stored and transported on conveyors to the post-shredder technologies. This comprises of a series of mechanical metal separation processes over band magnets, eddy current separators and trommel screen. During the process two size fractions of ≤ 30 mm and ≤ 150 mm of ASR are produced.

Figure 3.2 Shredding plant layout of case study site

Onsite monitoring of the facility was carried out over a three-month period. The mass balance of ELVs entering the facility and the output from the shredding plant was

recorded. The Duty of Care imposed on the organisation ensured that all ELVs brought on to site were weighed and all paperwork (e.g., consignment notes) complied with the requirements of the Environment Agency. ELVs were depolluted and dismantled prior to shredding therefore all fluids and tyres were removed.

3.3.2.2 Sampling procedure

Samples of ASR (for each fraction produced: ≤ 30 mm and ≤ 150 mm) were collected from a shredder plant over a four-day sampling period to ensure a representative feedstock through the processing plant. For each day 52 t of ASR was collected (total collected 208 t of ASR). Each day's sample was cone and quartered following both BS EN 932-1 (1997) and CM3820 (2009) procedures. This procedure was chosen, as it is ideal for large amounts of material [Allen, 1981]. This method initially starts with a heap (cone) of the material and is divided into 4 sections (quarters). The opposite quarters of the heap were rejected and the two remaining quarters were re-mixed and a smaller second heap formed. The process was then repeated until the required sample size was reached within one of the quarters. This produced a quartered sample of 200 kg per day. At the end of the four day period the accumulated daily samples were combined to produce an 800 kg sample. This sample was subsequently, crushed through a 50 mm screen using a Wagner Machienbau Gmbh Type WS30 45 kW crusher. The crushed sample was subjected to coning and quartering procedures (BS EN 932-1 (1997) and CM3820 (2009)) to produce four 12.5 kg homogeneous sample (ASR1 – ASR4). Each sample was subjected to further grinding down using 30k in-line Muffin Monster. This produced samples of ≤ 2 mm. Samples were then extracted from this for characterisation analysis.

For the pyrolysis trials of the ASR the 150 mm size fraction of ASR produced by the plant was crushed through a 15 mm screen using a UNTHA UK Type RS40-1000 shredder (shown in Figure 3.3). This ensured a homogeneous feed into the pyrolysis plant as shown in Figure 3.4.

Figure 3.3 Close-up view of a shredder used in a sample preparation for ASR pyrolysis trials

(a) (b)

Figure 3.4 Trial ASR material. (a) As received (AR): ≤ 150 mm; (b) Crushed & screened ≤ 15 mm

3.3.3 Pilot-scale test plant

Figure 3.3 shows the pilot-scale rotary kiln used for this study. The kiln comprised a stainless steel kiln, which was 3.5 m long with an internal diameter (ID) 0.38 m. This was surrounded by an externally heated gas fired furnace (up to 1100^{o}C) in four independent zones (total length 2 m) each with PID control. The feed hopper had a screw delivery capacity up to 100 kg hr^{-1} via an airtight closure system and rotation speed controller (inverter). The furnace temperatures were measured along the length via sensors connected to a data logger (Pico logger unit). The kiln rotation speed had a range of 1 to 12 rpm (to allow variable residence times in the hot zone), with slop angle

up to 10^{θ}. The system allowed the continuous char discharged from end of the rotary kiln into a sealed drum collecting the heaviest char (coarse) and the fine char collected at a subsequent point.

Figure 3.5 Pilot-scale rotary kiln test plant (based at Mitchell Dryers – CAD Works Engineering Ltd, Carlisle, UK)

In the pyrolysis tests, air inside the plant was removed by purging with nitrogen (flow rate of 10 l min^{-1}) which was injected below the feeding hopper. The rotation speed of the kiln was set at 2 rpm and the kiln slope angle of 1^{θ}. The kiln was heated at $5^{o}C\ min^{-1}$ up to the test pyrolysis temperature of (i) 800^{o}C, (ii) 900^{o}C and (iii) 1000^{o}C. The feeding of ASR started when kiln reached the pyrolysis temperature set point (e.g. 800^{o}C). Initial feeding rate of 10 kg hr^{-1} (inverter was set at power of 15%) was used. Each trial was run for 3 hours under these set conditions. Char was collected after each test, weighed and stored for chemical and physical analysis.

3.3.4 Analysis

3.3.4.1 Syngas analysis

Syngas samples for CO, CO_2, CH_4, C_2H_4, C_2H_6, H_2O, HCl, SO_2, H_2S, N_2, NO, NO_2, N_2O, NH_3 and HF, were obtained from a sampling port located at the side-access of the

horizontal exhaust flue-gas stream line and analysed by a high resolution multi-component Fourier Transform Infra-Red (FTIR) on-line gas analyser [Protea-Protir AFS/B2 Mobile FTIR analyser, Protea Ltd, Cheshire, UK]. The analyser is fitted with an integral sampling control system (i.e. controlled temperature and pressure) where the syngas has to pass through a pipe bounded by glass wool, filter, and a heated line (~180°C), in order to ensure that conditioned sample gases pass to the analyser. In addition, the FTIR contains an on-board electrochemical (zirconia-based) oxygen sensor. This allowed to analyse O_2 in the syngas and provides the pyrolysis system/trials with the ability to actively correct for zero oxygen content online. Furthermore, Syngas produced were collected in a Tedlar sample bags (dual stainless steel fittings – 3 l, purchased from SKC Ltd, UK) for further gas species identification. Figure 3.4 shows close up view of FTIR analyser with sampling control system (fitted into the horizontal exhaust sample port) as well as Tedlar bags.

Figure 3.6 Photographs of FTIR analyser fitted to the pilot-scale plant & Tedlar bags used for syngas samples

The calibration ranges of the species analysed by the FTIR instrument are reported in Table 3.2.

Table 3.2 Calibration ranges of the syngas species for the FTIR analyser

O_2	0-20.9%	C_4H_{10}	0-25%
CO_2	0-30%	HCl	0-2%
H_2O	0-40%	SO_2	0-4%
N_2	0-40%	H_2S	0-4%
CO	0-50%	NO	0-0.1%
CH_4	0-70%	NO_2	0-0.1%
C_2H_4	0-25%	N_2O	0-0.1%
C_2H_6	0-25%	NH_3	0-0.1%
C_3H_8	0-25%	HF	0-0.1%

The collected syngas by the Tedlar bags were examined via gas chromatography – high-resolution mass spectrometry (GC-MS, Agilent 7890, Agilent Technologies, Santa Clara, CA, USA) operated in selected ion monitoring mode with a splitless injection volume of 2.0 μl. The column used was a DB-5ms (J & W Scientific, Folsom, CA, USA); with dimensions of length, 30 m x 0.25 mm ID x 0.25 μm film thickness. The temperature programme used for the analysis was 35°C, held for 2 min, raised to 125^{o}C at the rate of 25^{o}C min^{-1}, then to 240^{o}C at a rate of 10°C min^{-1} and finally to 300^{o}C at the rate of 5^{o}C min^{-1}, with a final hold time of 20 min. The detector temperature was set at 280°C and helium was used as a carrier gas at a constant flow of 1 ml min^{-1}.

3.3.4.2 Raw ASR and pyrolysis solid residue (char) physical and chemical analysis

The gross calorific value (CV) was measured using a Parr 6200 Isoperibol bomb calorimeter (Scientific & Medical Production Ltd, UK) followed BS EN 15400 (2011), protocol.

Proximate analysis of the moisture, ash and volatile matter were determined according to British Standard methodologies of BS EN 15414 (2011), BS EN 15403 (2011), BS EN 15402 (2011), respectively. The moisture content was determined by drying samples in an oven at 80^{o}C for a 12 hr period. The ash and volatile matter (VM)

contents were determined from the percentage residues of the initial material which was combusted at 525ºC (±25ºC, BS EN 15403 (2011)) and 925ºC (±25ºC, BS EN 15402 (2011)), respectively. Fixed carbon was calculated to give a total of 100 (% by, weight) of the proximate analysis.

Ultimate analysis of S, C, H, N were carried out using CHNS-O Flash 2000 Organic Elemental Analyser (Thermo Scientific) followed method standard BS EN 15407 (2011) and BS EN 15408 (2011)). BBOT (2,5-Bis(5-tert-butyl-2-benzo-oxalzol-2-yl) thiophene, ($C_{26}H_{26}N_2O_2S$)) standard was used. The mass samples of the ASR or char were approximate 2-3 mg combusted at temperature of 850ºC.

Metals of Be, Na, Mg, Al, K, Ti, Cu, Mn, V, Zn, Mo, Cr, Ni, Ca, Fe, As, Se, Ba, Pb, Hg, Ag, Sb, Cd, Tl, Li and Au were analysed by inductively coupled plasma mass spectrometry (ICP-MS), method CEN/TS 15411 (2006). The samples were prepared after nitric acid microwave digestion programmed for 0-200ºC (in 10 min), held for 15 min and cooled down over a period of 35 min. Multi-element calibration standard-1, 10 $\mu g\ ml^{-1}$ (10,000 ppb) in 5% HNO_3, 100 ml (Agilent, USA) were used.

Morphological analysis of the ASR or char was carried out using Scanning Electron Microscope (SEM) equipped with X-ray Diffraction (XRD) analyses. The samples were prepared on the front face of 12.5 mm diameter, 6 mm pin length specimen stub. The stub samples were gold coated using Emitech K550X sputter coater and later placed into specific sample holder for examination. In EDX, elemental quant feature was used for C, N, O, Na, Mg, Al, Si, P, S, Cl, Ar, Ag, Cd, K, Ca, Ba, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Au, Hg, Tl, As, Pb and Br. In SEM, higher images magnifications scanning at 40x were preferred.

3.3.4.3 Toxic/Pollutant analysis of ASR and the pyrolysis solid residue

Polyaromatic hydrocarbon (PAHs) compounds were extracted from as received ASR and pyrolysis solid residues using ultrasonic enhanced solvent extraction based on the EPA 3550 method (2007). Anhydrous sodium sulphate (BDH, Poole, UK) was added to

a 5 g sample and extracted using ultrasonic extraction with a 50:50 mix of hexane/acetone. The extracts were examined by gas chromatography – high-resolution mass spectrometry (GC-MS, Agilent 7890, Agilent Technologies, Santa Clara, CA, USA) operated in selected ion monitoring mode with a splitless injection volume of 2.0 μl and quantified by comparison with a solution containing each of the targeted compounds. The column used was a DB-5ms (J & W Scientific, Folsom, CA, USA), with dimensions of length 30 m x 0.25 mm ID x 0.25 μm film thickness. The temperature programme used for the analysis was 40°C, held for 1 min, raised to 120°C at the rate of 25°C min^{-1}, then to 160°C at a rate of 10°C min^{-1} and finally to 300°C at the rate of 5°C min^{-1}, with a final hold time of 15 min. The detector temperature was set at 280°C and helium was used as a carrier gas at a constant flow of 1 ml min^{-1}. The results for each target compound were tabulated with CAS number, retention time, concentration and library fit. The GC-MS was calibrated prior tests and incorporates a 4 point calibration using standards (internal and surrogate) for sample quantification and quantifying procedural recovery. The calibration range extends from 0.08 mg kg^{-1} to 40 mg kg^{-1}. Any samples that are over-range were diluted with extraction solvent and re-run. R^2 values for each of the analytes were in excess of 0.99. Standards of 16 PAHs in a 80 mg l^{-1} mix solutions, deuterated PAH internal standard solutions (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) at 4,000 mg l^{-1} and surrogate standard solutions (2-fluorobiphenyl and 4-terphenyl-d_{14}) at 2,000 mg l^{-1} were obtained from AccuStandard Inc. (New Haven, CT, USA).

Polychlorinated Biphenyls (PCBs) were extracted using ultrasonic enhanced solvent extraction with a 50:50 mix of hexane/acetone. The extracts were dried using anhydrous sodium sulphate and reduced by evaporation to 1 ml. A sample of the extract was treated with concentrated sulphuric acid and copper granules to remove any interference from sulphur groups. The extracts were then analysed by gas chromatography equipped with an electron capture detector (GC-ECD, Agilent 7890, Agilent Technologies, Santa Clara, CA, USA) with a splitless injection volume of 2.0 μl. Separations were conducted using an HP-5ms capillary column (J & W Scientific, Folsom, CA, USA) with dimensions of length 30 m x 0.25 mm ID x 0.25 μm film thickness. The carrier gas was purified nitrogen at a flow rate of 1 ml min^{-1}. The GC-ECD conditions were as

follows: injector temperature 220ºC; detector temperature 300ºC; total time for one GC-ECD run 20 min; initial oven temperature 75ºC held for 3 min, increased to 150ºC at rate of 15ºC min^{-1}, then increased further to 260ºC at 6ºC min^{-1}, finally the temperature was increased up to 300ºC at 20ºC min^{-1} rate and held for 5 min. The individual congeners were then quantified against the standard congener reference solution (PCB 7 and PCB 12 congener suites). Aroclors were calculated from an Aroclor reference standard. Six-point calibration using standards sourced from traceable material were made. Calibration range extends to 400 μg kg^{-1}.

Total petroleum hydrocarbon (TPHs) used ultrasonic enhanced solvent extraction of a measured 5 g samples of ASR or solid residue. The resulting extracts were dried and then subjected to analysis based on EPA 8015D method (2003). The analysis was carried out by gas chromatography equipped with flame ionisation detector (GC-FID, Agilent 6890, Agilent Technologies, Santa Clara, CA, USA) had a splitless injection volume of 1.0 μl. The column used was a DB-5ms (J & W Scientific, Folsom, California, USA), with dimensions of 30 m x 0.25 mm ID x 0.25 μm film thickness. The temperature programme used for the analysis was 40°C, initially held for 1 min to 320°C at a rate of 10°C min^{-1}, with a final hold time of 40 min. The injection port and detector temperature were set at 300°C. The samples were placed in 2 ml screw top vials (Avonchem Ltd, Cheshire, UK). The analysis quantified by comparison with a solution containing diesel hydrocarbons. The C8-C40 result can be reported with banding, which breaks down the total TPH into smaller fractions, which are more specific, these include Diesel Range Organics (DRO), Gasoline Range Organics (GRO) and Mineral Oil Range Organics (MRO). Different organic solvents were used for calibration and extractions. The standard used for defining the diesel carbon range was diesel range organic mix, 99% pure (EPA/WISC) purchased from Restek Corporation (Bellefonte, PA, USA). The standard contained 10 compounds (decane, dodcane, tetradecane, hexadecane, octadecane, eicosane, docosane, tetracosane, hexacosane and octacosane). Whereas, GRO mix (9 components, includes: benzene, ethylbenzene, 3-methylpentane, naphthalene, toluene, 1,2,4-trimethylbenzene, 2,2,4-trimethylpentane (isooctane), m-xylene, *o*-xylene) and MRO (standard mix C18-C32) were used. A 5

point calibration using standards sourced from traceable material. Calibration range extends to 40000 mg kg^{-1}.

Benzene, toluene, ethylbenzene, xylenes (BTEX) analysis used ultrasonic enhanced solvent extraction (explained previously) of an accurately weighed of 5 g samples of ASR or solid residue was developed on the basis of the EPA 3810 (1986) and 8015D methods (2003). The extracts (1.0 μl) were injected into the GC-FID (Agilent 6890, Agilent Technologies, Santa Clara, CA, USA). A fused-silica megabore column (J & W Scientific, Folsom, California, USA) DB-642 (6% cyanopropylphenyl-94% dimethylpolysiloxane; 75 m x 0.53 mm i.d. x 3.0 μm film thickness) was employed. The carrier gas was purified helium at a flow rate of 10 ml min^{-1}. The GC-FID conditions were as follows: injector temperature 180^{o}C; detector temperature 220^{o}C; initial oven temperature 30^{o}C held for 1 min, increased to 100^{o}C at rate of 5^{o}C min^{-1}, then directly to 220^{o}C at 8^{o}C min^{-1}, then held for 5 min. Certified standards of BTEX and MTBE mix at 2000 μg ml^{-1} (7 component, includes: benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, methyl tert-butyl ether), purchased from High-Purity Standards (Charleston, SC, USA) were used. Quantification was achieved by the use of a seven-point calibration curve from 0.0 μg ml^{-1} to 480 μg ml^{-1}. R^2 values for each of the analytes were in excess of 0.99.

Total organic carbon (TOCs) was analysed for ASR and solid residue based on methods reported previously [Heron et al. 1997; Schumaccher, 2002]. 0.25 g of air-dried and ground sample (crushed to a particle size of less than 212 μm) was mixed with 10 ml of concentrated sulphurous acid in a 50 ml digestion tube. This was warmed to 40°C for 14 hr. The resultant mixture was then heated to dryness at 100°C. The dried residue was analysed for carbon content using an ELTRA induction furnace fitted with a nondispersive infrared (NDIR) cell (CS-800, ELTRA GmbH, Germany). In this instrument, the sample was combusted at 1600°C in an oxygen atmosphere, the combustion gases then passed through an infrared cell, which measured the carbon dioxide concentration. The total quantity of carbon liberated was calculated and reported as a percentage of the original mass of sample. The method was calibrated every day and incorporates a 5 point calibration (including blank) using matrix matched

standards (CWW-TOC-A 5 mL) purchased from High-Purity Standards (Charleston, SC, USA) sourced from traceable material. The calibration range extends to 12.5%. Any samples that were over-range were re-extracted with reduced sample weight and re-analysed.

Loss on ignition (LOI) at 450^{o}C determines the percentage by mass of the solids samples that is either burnt or decomposed when it is heated in air to a set temperature. This value is used as an estimate of the amount of organic matter in the samples. Sample preparation used an air dried and ground of samples (5 g) that has been grounded to nominally 212 μm. Analytical was then applied by the dried (for 2 hr) and ground samples were weighed and heated in a furnace (Lenton Furnaces & Ovens, Hope Valley, UK) to the required temperature. It is then removed from the hot furnace and placed in a desiccator to cool for at least 60 min. The crucible and residue were weighed again and the loss on ignition was calculated from the loss in mass of the sample using KERN ABT-320-4NM balance (ABT – KERN & SOHN GmbH, Balingen, Germany).

For pHs analysis, sample preparation used a 10.0 g whole of the ASR (as received) or 10.0 g of solid residue samples were mixed with 25 ml of deionised water in a 60 ml plastic bottle (method standard BS 6068 (1986)). This samples were then shaken for 15 min. pH of the suspension was measured using a Jenway Model 3510 pH meter (Jenway, Staffordshire, UK) fitted with a combination pH electrode and a temperature sensor. Results were automatically corrected for temperature by the meter. Prior to analysis the meter was calibrated at 3 fixed points at approximately pH 2.0, 7.0 and 13.0. The buffers used are commercially available buffers (purchased from Camlab Ltd, Cambridge, UK) which have been assigned values by comparison with NIST traceable buffers.

3.4 Summary

Methodology studied in this research in order to achieve aims, objectives and scope of work has been summarised below.

Production of ASR at case study: The shredder plant (Northwest, UK), undertook trials to assess plant's efficiency, mass balance, metals recovery and ASR production. Representative samples of ASR were collected and subjected to cone and quartered procedure according to a standardised methodology (EN 932-1 (1997) & CM3820 (2009)). Samples for analysis were thoroughly mixed by grinding down to ≤ 15 mm and ≤ 2 mm samples.

ASR characterisation: Blank extraction samples, repeated samples and standard reference solution mixtures were processed along with the ASR samples to reduce sampling errors and assure reproducibility of the results. Samples were prepared for physical and chemical analysis. Prior to analysis samples were digested in a microwave digester. This method proved superior in both the quantity and the precision obtained compared to other programme digestion techniques investigated.

Pilot-scale experiments: The pyrolysis of ASR in a pilot-scale reactor facility (100 kg/hr) with a different pyrolysis conditions were investigated. The syngas from these experiments was analysed using Fourier-transform Infrared Spectroscopy (FTIR) analyser and Tedlar sample bags for gas species identification (using GC-MS). By-product char (in fine and coarse structure) from ASR pyrolysis were analysed for CV, proximate, ultimate and toxic/pollutant measurements.

Assessment of commercial thermal technologies worldwide with a production capacity (kg hr^{-1}): A criteria list for companies of the thermal processing plants available globally was developed. All types of feasible thermal processing of ASR or biomass for electricity generation was reviewed for the period (1992-2018).

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Introduction

This chapter describes the viability of post-shredder technologies (PST) worldwide using thermal treatment (pyrolysis and gasification) and experimental data based on the pyrolysis of ASR.

Lists of worldwide companies which have or claim to have commercialised thermal treatment plants and experimental measurements (including ASR production and characterisation, ASR pyrolysis behaviour, syngas emissions and char investigations) are reported, studied and discussed.

Part of this work has already presented (oral or poster) and a journal article published (see list of publication in Appendix D).

4.2 Commercial assessment of the thermal technologies

Table 4.1 lists examples of worldwide companies, which have or claim to have commercialised/marketed thermal treatment plants for pyrolysis or gasification. The study concentrated on commercial scale plants and therefore did not consider pyrolysis and gasification from universities, research institutions. From the review of companies and their technology selected number were identified as potential solutions to ASR disposal. The criteria for rejection were as follows:

- Feedstock that technology can use was not applicable – company unable to process ASR
- Technology no longer promoted – either due to economic or technical problems

Example of the deselected/rejected companies with a thumbnail profile for each and reasons are shown in Appendix A. Those that passed the initial sort were then evaluated against the criteria (shown in Table 3.1). A second round of evaluation was then undertaken looking at the economic methods of the process. The results revealed that many organisations did not have robust economics for their process or lacked detail

designs. This was reflected in there being limited documentation of operating thermal plants using ASR. Workers in this area [Vermeulen et al. 2011; Cossu & Lai, 2015] who have listed both experimental technologies and full-scale applications concluded that research was required to prove the long-term prospect of thermal treatment of ASR. The organisations in Table 4.1 were sub-divided into the capacity of their plants. It can be seen that plants between 10-1000 kg hr^{-1} mostly used biomass material and were intended for small heat capacity applications. As the capacity size increased over 1000 kg hr^{-1} the plants tended to use more plastic derived waste. This was closer to the composition of ASR and therefore would potentially offer a thermal processing solution. Example of the advertise pyrolysis companies (with focus on plastic feedstock) and been contacted are presented in Appendix A. All the companies listed in Table 4.1 were contacted by email and where available additionally by telephone. Those based in the UK and still operational were visited.

The shredding industry finds itself having to make investments in un-proven technologies with limited economic data to justify such a move. In contrast those organisations with new thermal processes have yet to prove that ASR is a viable feedstock with many citing the variability of composition presenting challenges to their process. This support the view and the highlighted points of EPRS, (2016) that in practice moving towards a more circular economy would face a number of barriers and challenges. These would include financial (for businesses, in particular the cost of small and medium-sized enterprises); key economic enablers (lacking, inter alia, pricing systems encouraging efficient resource reuse and reflecting full environment costs); skills and multi-level governance (i.e. action required at many levels (e.g. international, European, national, local)). By utilising ASR as a potential fuel source and recovering metals and glasses which would normally be lost; there is an opportunity for the recycling sector to support the meeting of the ELV Directive.

In order to achieve ambitious policy targets settled by the ELV Directive on recycling, recovery and reuse, innovative integrated technologies need to be developed. Yet challenges, no developers of new technologies worldwide were able commercially and technically proven the recovery of energy from ASR.

Table 4.1 Worldwide pyrolysis & gasification commercial companies

Company/Plant Owner	Country	Feedstock	Capacity (kg h^{-1})
2 G BioPOWER Ltd	UK	Tyres	nd (not disclosed)
ANDRITZ Carbona	Finland	Wood	nd
Babcock & Wilcox Volund	Denmark	Wood, agricultural, RDF	nd
Balboa Pacific Corporation	USA	Waste	nd
BTG Biomass Technology Group	Netherlands	Biomass, waste	nd
Future Blends Ltd	UK	Biomass	nd
Radhe	India	Biomass	nd
TK Energi AS	Denmark	Biomass	nd
NREL	USA	Biomass	10
VTT	Finland	Wood	10
FCIPT	India	Medical waste	20
RTI	Canada	Biomass (wood)	20
TNO	Netherlands	Biomass	10-30
Bio-alternative	Switzerland	By-product oil	50
GTRI	USA	Wood	50
Pyrovac	Canada	Biomass (softwood bark)	50
Daekung ESCO, Ltd	Korea	Oil palm EFB, pine, kelp	41-83
Metso-UPM	Finland	Biomass	100
Union Fenosa	Spain	Wheat straw, pine, wood	150
Agritherm	Canada	Sawdust, oil seed, bagasse	200
Egemin	Belgium	Wood	200
Renewable Oil Int.	USA	Biomass (various)	200
Biomass Eng. Ltd	UK	Biomass (sawdust)	250
C.A.R.E. Ltd	UK	Biomass, waste	5-250
PYTEC Thermochemische Anlagen GmbH	Germany	Wood, pine wood, wheat straw	250
Ensyn	Canada	Agriculture	400
GRES	Greece	Wood, sawdust, forest residues	400
RESEM	Taiwan	Plastic (PE, PP, PS, ABS, Nylon)	200-400
Alten	Italy	Wood, agriculture	500
FZK	Germany	Straw	500
Lurgi LR	Germany	Biomass	500
Wellman Process Eng. Ltd	UK	Wood chips	250-500
Anhui Yineng Bio-energy Ltd	China	Biomass, sewage sludge	600
Beston	China	Mixed plastics	250-800
Shree Balaji Eng. Works	India	Waste plastics, tyres, wood	250-800
Cynar PLC	UK	Plastic (HDPE, LDPE, PP, PS)	~ 416, 833
ENEA	Italy	Biomass (wheat straw)	1000
EPI Ltd	UK	Plastic, MSW, medical waste	1000
Get Energy Prime	Italy	Plastics	200-1000
BTG	Netherlands	Palm (EFB)	2000
Pyrocrat	India	Mixed plastics, carry bags, bottles	125-2000
ABRI-Tech INC.	Canada	Agriculture	2083
CHO Power	France	Biomass, waste	3000
Biogreen	France	Plastics, tyres, MSW, biomass	~ 3300
VER GmbH	Germany	Biomass	3500
Eqtec	Spain	Biomass, waste	4000
Hudol Ltd	Wales, UK	Biomass, plastics	4000
Vulcan	USA	Biomass, MSW, agriculture	4000
HoSt	Netherlands	Biomass, waste, sludge	1000-5000
Dynamotive	Canada	Agriculture	8000
Ebara	Japan	Plastics, biomass, sludge, MSW	8125
Fortum	Finland	Wood, forest residues	10000
Splainex	Netherlands	Plastics, biomass, tyres, MSW	Up to 21000
PRM Energy Systems Inc.	USA	Rice husk straw	~ 1250-83333
Chinook Sciences	UK	MSW, biomass, RDF, industrial waste, yard waste	~ 4166666
Anergy Ltd	UK	Waste, biomass	Pilot - Industrial
Enerkum	Canada	Wood, peat, straw, MSW	Pilot - Industrial
A.H.T. Vertriebs GmbH	Germany	Rice husks, wood	Industrial scale
Feeco International	USA	Biomass, waste	Industrial scale
Grubl Automatisierungstechik GmbH	Austria	Wood	Industrial scale
Klean Industries	Canada	Tyres, plastics, MSW, medical waste	Industrial scale
Torftech Energy Ltd	UK	Food, biomass, waste, chemicals	Industrial scale

4.3 Experimental exposures

4.3.1 ASR characterisation

Figure 4.1 shows the mass balance of ELVs entering the site over study period. The amount of material recovered from the ELVs was 70% ferrous metals, 3% non-ferrous metals (heavy materials were called Zorba, other materials produced; stainless steel, copper meatballs and wires) and formation of 26% ASR. The results are below the ELV Directive targets, which is a concern for the automotive industry, which is required to meet these. However, these results are similar to other reported work [Morselli et al. 2010; Fiore et al. 2012]. During the process two size fractions of ≤ 30 mm and ≤ 150 mm of ASR production were formed. ASR ≤ 150 mm size fraction represents 75% of the total ASR, with the ≤ 30 mm fraction making up the remaining 25%. The plant produced 70 t of ASR per day, which required processing and final disposal to landfill. The current charge for landfilling ASR (September 2016) is €114 per tonne. Therefore, there is an opportunity to recover this material and meet both the ELV Directive and goals of the circular economy package.

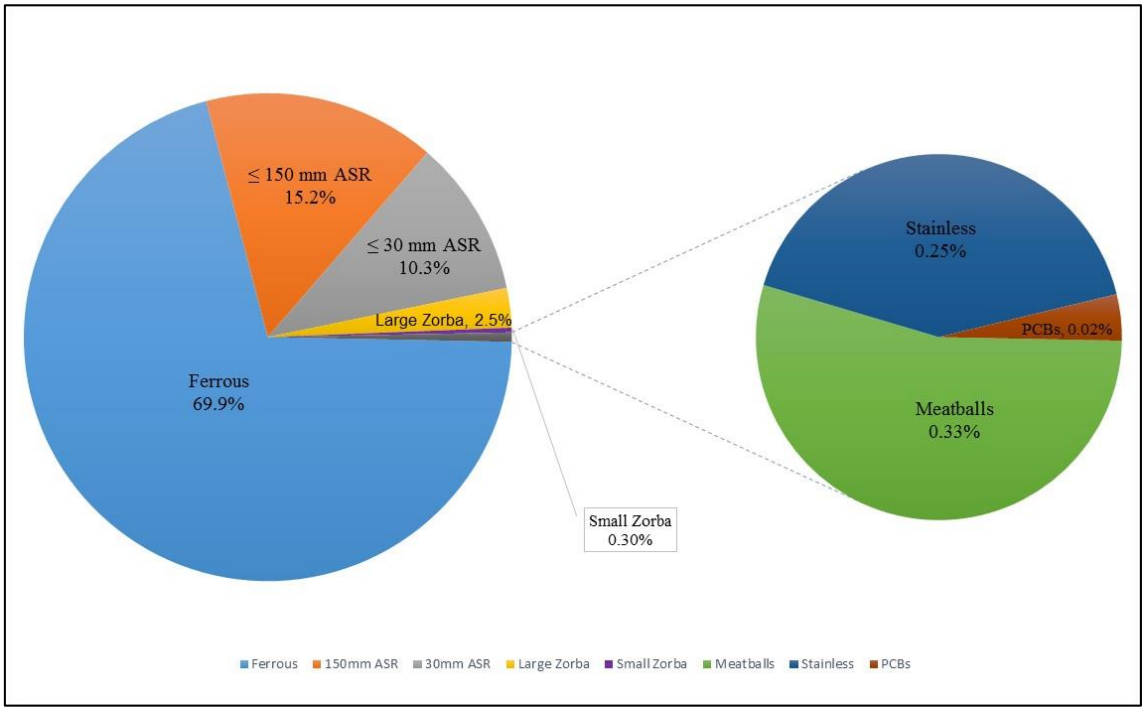


Figure 4.1 Shredding plant (case study) mass balance

Table 4.2 shows the result of ASR 150 mm material type compositions. It was possible to identify glass, plastics, textile, foam, rubber, wood, cork, wiring/electrical, paper, cardboard blended together and/or with soil and dust/dirt. The metal content was very low and was combined into the fines (≤ 5 mm) and difficult to separate. The mixed plastics accounted 47% by weight, whereas, the textile fraction was 11% by weight, (similar percentages reported by Mallampati et al. (2017) and Lin et al. (2010)). Textiles together with polyurethane foam (PUF) and cork are derived from car seats and interior carpeting. The rubber contents, mostly from hoses, ranged from 8% to 23%. The fines fraction was 7% by weight and supported Harder & Forton, (2007) study that this was difficult to break down into quantifiable materials.

The variability in particle size distribution for the ≤ 150 mm post additional shredding is shown in Table 4.3. It can be seen that ≥ 90% of the ASR was smaller than 30 mm. This is in contrast to the larger size 40-50 mm representing < 1%. However, size 30-40 mm includes a large amount of PU foam, which included embedded small fraction of plastics, glass and fines. The size distribution represents the mechanical properties of the different materials, with the brittle polymers ending up in the ≤ 30 mm fraction.

Table 4.2 Materials composition (% of total mass) of the ASR quarter procedure

Materials *(%wt)*	**ASR 1**	**ASR 2**	**ASR 3**	**ASR 4**
Plastic	47.88	45.21	51.67	42.97
Foam	2.94	2.93	2.70	2.21
Rubber	15.88	17.65	8.24	23.61
Textile/fabric	10.35	8.65	12.23	10.61
Cork	11.05	14.76	13.22	12.86
Wood	1.17	1.34	0.64	1.53
Wiring/electrical	1.76	2.10	1.76	0.14
Glass	0.82	0.63	0.93	0.53
Paper	0.47	0.31	0.38	0.26
Cardboard	0.23	0.01	0.56	0.90
Dirt	0.35	0.29	0.41	0.27
Fines (e.g. soil- not blended)	6.57	5.00	6.01	3.02
Metals*	0.47	1.10	1.24	1.10
Others	0.06	0.02	0.01	0.00

Keys: [fine metals caught into a soil/dirt, hard to separate]*

Table 4.3 ASR particle size distribution (subjected prior materials separation)

Size Fraction	**Result (%wt)**
< 2 mm	< 1
3 – 15 mm	40
16 – 30 mm	50
30 – 40 mm	10
40 – 50 mm	< 1
> 50 mm	< 1
Total	100

The characterisation of ASR in term of calorific value, proximate and ultimate compositions are presented Table 4.4. The gross calorific value range from 16.3-23.5 MJ kg^{-1} expressed the variation on the sample compositions. This was due to sampling error resulting in more polymer rich samples than others. It is interesting to see that the copper content was low; this was mainly due to the post-shredder technologies removing copper. This particular ASR is therefore, better suited for energy recovery as it does not contain high levels of copper which acts as a catalyst for dioxin formation. Another added benefit of the composition is the low chlorine levels (related to the removal of electric cables) reducing the potential for dioxin formation further. The sulphur content of 0.20%, by weight is similar to other studies reported [Mancini et al. 2010; Kameda et al. 2009; Saxena et al. 1995]. The concentrations of some metals presented in this ASR such as Ni, Cu and Hg were less than those reported previously [e.g. Mallampati et al. 2017]. Other elements like C, H, O, N, Pb, Mn, Cr, Tl their concentrations within the range reported by Sakai et al. 2014 and Cossu et al. 2014 in their literatures reviewed of ASR properties.

The results obtained from the organic pollutants analysis conducted on the ASR are presented in Table 4.5. Criteria for landfills for inert waste, stable non-reactive waste and non-hazardous waste (transposed from [Council Decision annex 2003/33/EC]) are reported Table 4.6. It can be observed that the amount of oils and organic contaminants detected in ASR sample were within the limit values apply to non-hazardous waste accepted criteria. Mancini et al. (2010) and Morselli et al. (2010) reported higher amount of mineral oils contents in the ASR obtained from Italian shredder industry of 22.3 g kg^{-1} and 26.8 g kg^{-1}, respectively. This may be to the depolluted and dismantling

technologies applied to the ELVs at a specific shredder industry. The concentration of the PCB in our study was similar to the Santini et al. (2012) study of 0.008 mg kg^{-1} value. Whereas, Viotti et al. (2010), Morselli et al. (2010), Mancini et al. (2010) and Cossu, (2014) detected PCBs concentrations of 2.97, 5.3, 7.9 and 44.45 mg kg^{-1}, respectively. The contaminants of TOC, BTEX, LOI and PAHs in the ASR were not reported in the literature for comparison to this study results.

Table 4.4 ASR particle size distribution (subjected prior materials separation)

	Units	**Results**
Calorific value		
CVgross	kJ kg^{-1}	16300 - 23500
Proximate analysis		
Moisture	%wt	22
Ash	%wt	20
Volatile matter	%wt	53
Fixed carbon	%wt	5
Total	%wt	100
Ultimate analysis *(AR)*		
Carbon	%wt	28
Hydrogen	%wt	3
Nitrogen	%wt	2
Oxygen	%wt	14
Sulphur	%wt	0.2
Chlorine	%wt	0.3
Metals *(AR)*		
Copper	mg kg^{-1}	7
Mercury	mg kg^{-1}	< 1
Cadmium	mg kg^{-1}	< 1
Thallium	mg kg^{-1}	< 1
Antimony	mg kg^{-1}	12
Arsenic	mg kg^{-1}	< 1
Chromium	mg kg^{-1}	16
Cobalt	mg kg^{-1}	< 1
Lead	mg kg^{-1}	56
Manganese	mg kg^{-1}	24
Nickel	mg kg^{-1}	7
Tin	mg kg^{-1}	< 1
Vanadium	mg kg^{-1}	< 1

Table 4.5 Pollutants analysis of the research studied ASR

Parameter	Result
TOC (%w/w)	0.26
LOI (%w/w)	1.39
BTEX (mg kg^{-1})	< 0.01
PCBs (7 Congeners) (mg kg^{-1})	< 0.01
Mineral oil (C10-C40) (mg kg^{-1})	7.7
PAHs (Total Speciated) (mg kg^{-1})	6.1
pH	7.20

Table 4.6 Criteria for granular waste acceptable at landfills (Transposed from Council Decision annex 2003/33/EC)

Parameter	Inert waste landfill	Stable non-reactive / non- hazardous	Hazardous waste landfill
TOC (%w/w)	3	5	6*
LOI (%w/w)			10*
BTEX (mg kg^{-1})	6		
PCBs (7 Congeners) (mg kg^{-1})	1		
Mineral oil (C10-C40) (mg kg^{-1})	500		
PAHs (Total Speciated) (mg kg^{-1})	100		
pH		> 6	

Keys: [Either TOC or LOI must be used for hazardous wastes]*

4.3.2 ASR pyrolysis pilot-scale (rotary kiln) trials

4.3.2.1 Pyrolysis behaviour/efficiency

Figures 4.2 shows an example the profile of initial heating and test temperature inside the kiln (test (iii) 1000^{o}C) indicating two and half-hours of stable ASR pyrolysis. At the end of the test, the furnace was turned off and allowed to cool.

4.3.2.2 Bio-oil pyrolysis by-product

The test rig was set up so as to minimise the production of oil. The unit was operated at 800-1000^{o}C which ensured that the material was converted to ash or syngas. Some residue was found on the char but this was minimal. No oil was observed downstream of the pyrolyser unit.

4.3.2.3 Syngas pyrolysis by-product

The analysis of the syngas output of the pilot-scale ASR pyrolysis trials detected by FTIR and GC-MS are presented in Table 4.7. The major gas species detected by FTIR were CO, CH_4, CO_2, C_2H_4, C_2H_6 and H_2S for all the pyrolysis temperatures studied. Similar results reported previously [Day et al. 1996; Galvagno et al. 2001], However lower concentrations of the species mainly CO, CO_2 and CH_4 were obtained in Galvagno et al. 2001 study due to the lower pyrolysis temperatures used (range within 550-680^{o}C). In addition, the CO/CO_2 ratio increases with temperature are in agreement with previous studies [Galvagno et al. 2001; Notarnicola et al. 2017]. Low N_2O and NH_3 emissions were achieved for all different temperatures pyrolysis of concentrations $\leq$ 0.01%vol. This was from the feeding. As a, result the pyrolysis environment were adopted to have the percent volumes of N_2 output of 10.0%vol. Whereas, the H_2O output of the experimental pyrolysis were in the range of 3.8-9.0%vol, may be to the factors such as fuel moisture content could have changed during storage, proper mixing of solid fuels particles, residence time, pyrolysis zone temperature, tar content, type of feeding or the cooling effects of excess air should also be taken into consideration. It is interesting to notice that no HCl detected for all the pyrolysis temperatures studied.

Benzene, propylene, 1,3-Butadiene, toluene, pentane and o-xylene were the abundant minor gases species identified by GC-MS with concentrations of $\leq$ 0.1%vol, which in agreement with the results obtained by Day et al. 1996. Mass spectrum examples of the minor gases species detected by GC-MS can be seen in Appendix B.

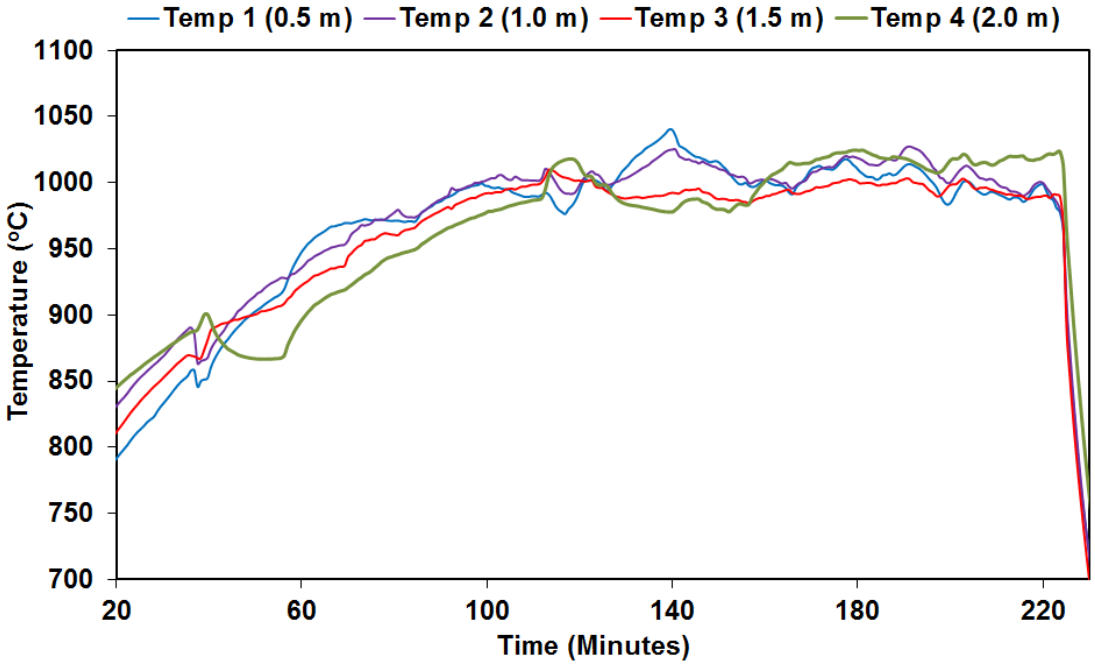


Figure 4.2 Profile of steady state temperature at the pilot-scale rotary kiln during ASR pyrolysis (including initial heating process). Heated zone represent distance from feed in heated zone

Table 4.7 Syngas output of the ASR pyrolysis pilot-scale trials

T (°C)	CO (%vol)	CO_2 (%vol)	CH_4 (%vol)	C_2H_4 (%vol)	C_2H_6 (%vol)	H_2S (%vol)	H_2O (%vol)	N_2 (%vol)	N_2O ppm	NH_3 ppm
800	16.3	5.2	10.2	1.4	1.8	3.2	8.3	10.0	42.0	137.5
900	17.3	7.4	6.0	0.3	0.5	2.9	3.8	10.0	38.1	122.1
1000	19.6	9.3	3.3	0.7	0.2	3.1	9.0	10.0	34.0	101.4

Components detected by GC-MS (≥ 0.1%vol)	**Formula**	**Molecular weight**
Propylene	C_3H_6	42
1, 3-Butadiene	C_4H_6	54
2-methyle-1, 3-butadiene	C_5H_{10}	70
Pentane	C_5H_{12}	72
Benzene	C_6H_6	78
Cyclohexene	C_6H_{10}	82
Toluene	C_7H_8	92
Styrene	C_8H_8	104
o-xylene	C_8H_{10}	106
Azulene	$C_{10}H_8$	128
2,5-Dihydroxybenzoic	$C_7H_6O_4$	154
Others*		

*Key: [* Not certain or detected but not listed, had concentrations ≤ 0.001%vol]*

4.3.2.4 Solid residue (char) pyrolysis by-product

The calorific value, proximate analysis and the metals content of the by-product pyrolysis char (fine and coarse) are presented in Table 4.8. Close-up view of the solid residue products in their tow fractions are shown in Appendix C. The volatile matter content of the ASR char in fine formation decreases as the temperature of the pyrolysis increases. Whereas, the fixed carbon contents of the char correlated with the temperature, similar to other reported studies [Galvagno et al. 2001; Haydary et al.

2016; Notarnicola et al. 2017]. The ash contents also correlated with the pyrolysis temperature. However, ash contents in the pyrolysis char-fine were very low compared to char-coarse at all pyrolysis temperature studied. The calorific value of the char-fine formation at 800ºC, 900ºC and 1000ºC range from 17.0-27.7 MJ kg^{-1}, 16.3-26.3 MJ kg^{-1} and 15.6-23.8 MJ kg^{-1}, respectively. Zolezzi et al. (2004) reported that the same relationship between lower calorific value of the char and the pyrolysis process temperature. The calorific value of the ASR pyrolysis char in the coarse forms only perceived at char coarse 800ºC. Galvagno et al. (2001) explained that the calorific values are influenced by the content of the hydrogen in the char. Figure 4.3 presents the C, H, N and S organic elements of the chars (fine and coarse) produced from the pyrolysis process. It is clear that the hydrogen contents in the char-coarse at 800ºC are higher compared to char-coarse at 900ºC and 1000ºC. In contrast with nitrogen content which had higher concentrations in the char-fine fractions. The sulphur contents in all char samples were minimal with highest value of 1.05% reported at char 800ºC-fine. This is related to the low content of the sulphur (0.2%) in the raw ASR feedstock (as shown in Table 4.4).

Table 4.8 Proximate analysis, calorific value & metal contents of the char products (fine & coarse) at various temperatures

Parameter	Pyrolysis char					
	800ºC -Fine-	800ºC -Coarse-	900ºC -Fine-	900ºC -Coarse-	1000ºC -Fine-	1000ºC -Coarse-
HHV (kJ kg^{-1})	17063-27741	2378-4189	16317-26309	Not-detected	15681-23895	Not-detected
Moisture (%wt)	0.48	0.02	0.23	0.04	0.47	0.01
Ash (%wt)	31.65	75.40	17.03	82.41	10.76	92.89
VM (%wt)	45.43	19.14	27.02	17.52	23.01	6.30
FC (%wt)	22.44	5.44	55.72	0.03	65.76	0.80
Metals (mg kg^{-1})						
Ca	23120.8	47282.1	14613.9	54340.6	21224.0	57274.5
Co	37.5	72.5	5.8	113.0	8.6	100.4
Al	5400.5	228617.1	1355.6	1116575	1886.4	143409.3
Cr	2343.4	2857.7	65.9	27390.1	161.9	12715.5
Mg	18772.5	30527.5	3238.9	19560.4	3723.5	23746.2
Fe	930.9	38393.2	1848.3	48241.7	2639.6	50475.7
Ni	201.7	3800.9	163.6	64139.1	470.5	14013.8
Cu	600.5	28864.9	709.4	15018.3	877.8	19444.9
Zn	5617.5	2865.7	11139.7	9542.1	8693.9	6296.3
Pb	670.3	297.2	2242.6	481.5	1832.1	349.7
V	16.5	52.3	2.7	66.1	4.4	44.9

Multi-elements calibration was applied before the analysis for QA of ICP-MS method over the concentration range 0.0 – 1000 ppb (6 points). Outcome example include SD and %RSD for each element (with calculation formula used) are shown in Appendix C. The most abundant metals of the pyrolysis chars (as shown in Table 4.8) were calcium, manganese, aluminium, chromium, lead, iron, nickel and zinc. The element contents of iron, calcium, nickel, aluminium and copper were higher in the char-coarse compared to the char in the fine formation. The copper was low in all char products in contrast to other reported studies such as Day et al. (1996) and Notarnicola et al. (2017). This was mainly due to the copper contents in their original ASR (feedstock) are much higher compared to the raw ASR feedstock used in this study.

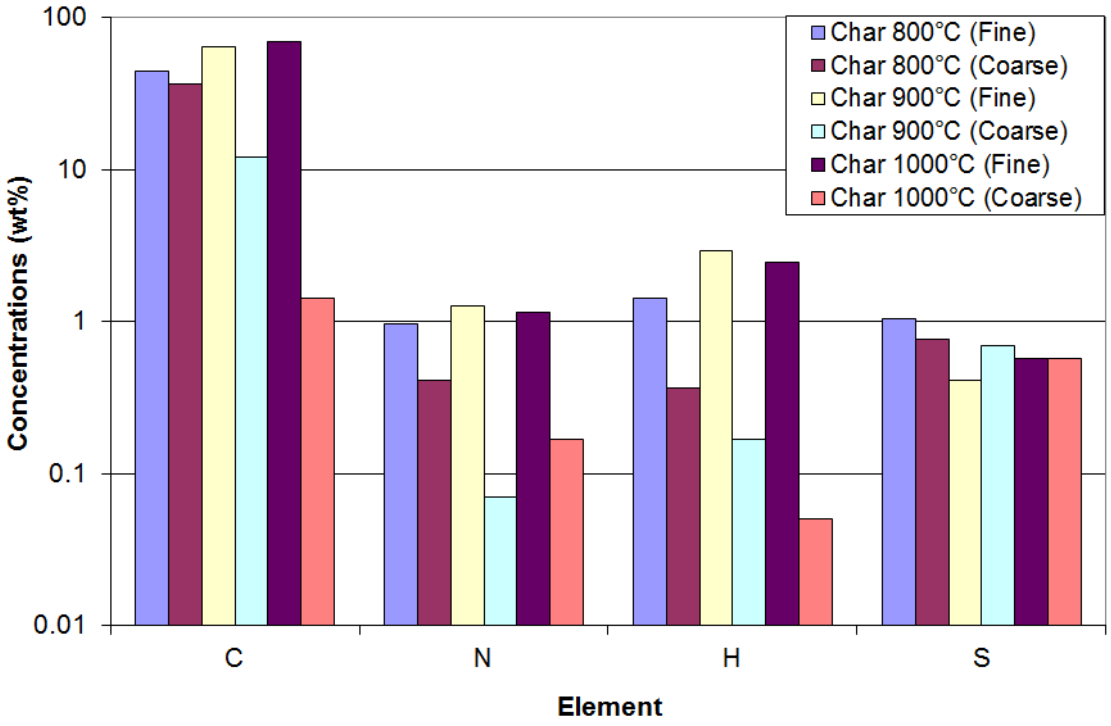


Figure 4.3 Organic elemental analysis of the ASR pyrolysis char generated at various temperatures in fine & coarse formation

Figure 4.4(c) and 4.4(e) show that the char-fine produced at the highest temperatures 900^{o}C and 1000^{o}C has smaller pores than char-fine at 800^{o}C. At the lower temperature the molecules, which volatilise have higher molecular weight and will create larger holes on the char surface [Notarnicola et al. 2017]. The images of char-coarse resulted a silicate type of structure in particular char-coarse at 1000^{o}C (Figure 4.4(f)) due to the mixed materials of fines presented.

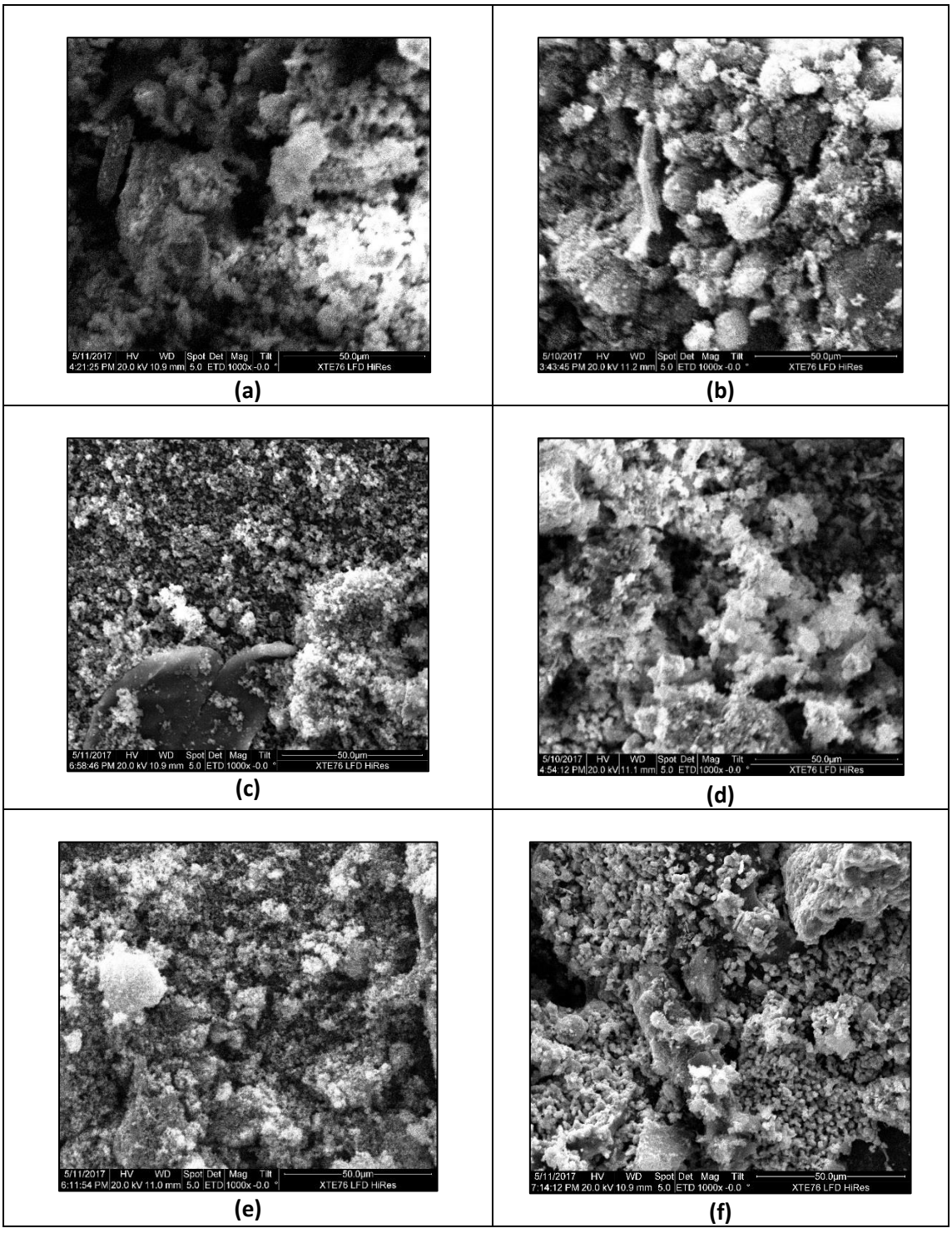


Figure 4.4 SEM images of the ASR pyrolysis char generated from pilot-scale kiln. (a) Fine char at 800^{o}C; (b) Coarse char at 800^{o}C; (c) Fine char at 900^{o}C; (d) Coarse char at 900^{o}C; (e) Fine char at 1000^{o}C; (f) Coarse char at 1000^{o}C

Figure 4.5 shows the EDX elemental compositions of the char products formed in both fine and coarse fractions. The figure reveals varying concentrations of carbon, nitrogen,

oxygen, aluminium, silicon, calcium, sulphur, potassium, zinc, cooper, iron, lead and bromine among char-fine and char-coarse. The lowest percentage of O_2 resulted at char-fine 1000^{o}C of 2.91%, in agreement with other study [Haydary et al. 2016] reported the effect of the pyrolysis temperature on the oxygen content of the char. The levels of chlorine in the chars were very low due to low contents of Cl presented in the raw ASR feedstock (Table 4.4). The commercially produced raw ASR was subjected to mechanical post-shredder technologies, which removed the electric cables [Khodier et al. 2018]. The elemental analysis results by EDX confirmed the other metals analysis procedure used in this study. For example, the carbon concentration of the char-fine at 800^{o}C, char-fine 900^{o}C and char-fine 1000^{o}C by EXD analysis were 45.93%wt, 50.56%wt and 56.25%wt, respectively. This correlation mirrored the results found in the carbon concentrations of char-fine at 800^{o}C, char-fine 900^{o}C and char-fine 1000^{o}C by CHNS-O organic analyser (Figure 4.3) of 44.87%wt, 64.82%wt and 69.18%wt respectively. The higher concentrations of iron found by ICP-MS in char-coarse for all the test temperatures studied: this was similar the results recorded by EDX.

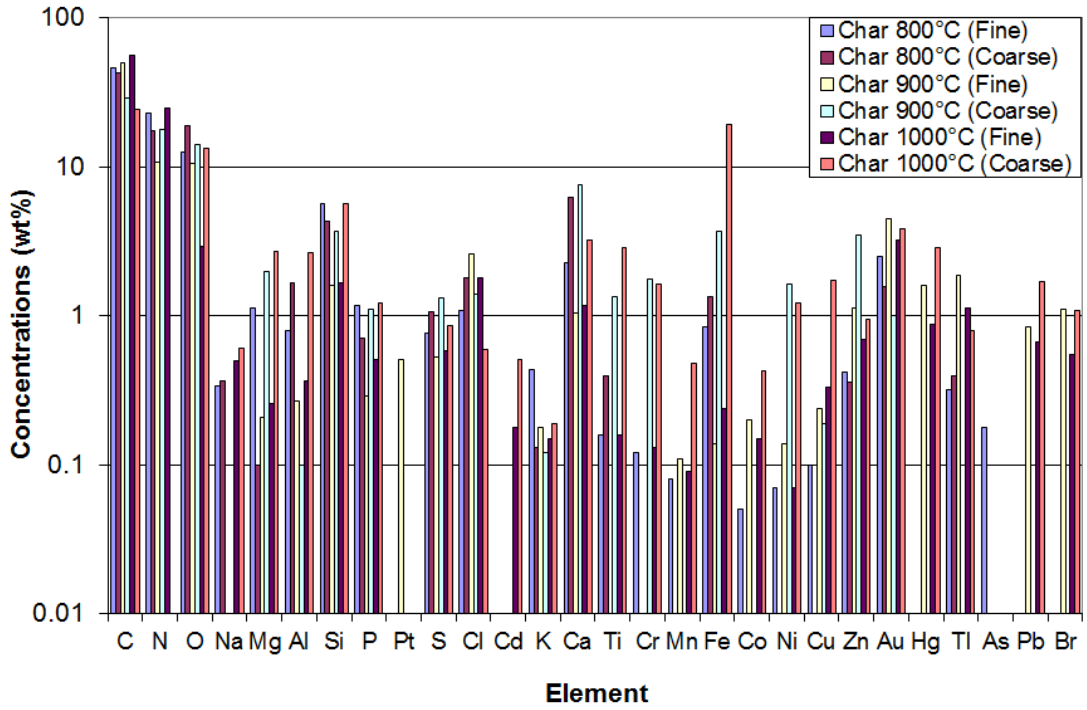


Figure 4.5 EDX analysis of the ASR pyrolysis char generated at various temperatures in fine & coarse formation

The toxic/pollutant analysis of the char was performed only on the fines fraction because of pervious findings of the inert nature of the coarse char structure (mineral ash and metals), detailed above. The PAHs content in solid residue (char fine structure) obtained at various temperatures are presented in Table 4.9. The maximum total concentration of PAHs was detected in solid residue produced at 800^{o}C ASR pyrolysis, with naphthalene and phenanthrene as the most abundant compounds. Similar results of the abundant compounds were noticed in Day et al.'s 1999 study of PAHs in ASR pyrolysis solid residue extracted at 750^{o}C. Whereas, fluoranthene and pyrene were the greatest abundant compound in the solid residue produced at 1000^{o}C with concentration of 879 and 1250 mg kg^{-1}, respectively. The concentration of the total PAHs detected in our study were higher than the values reported in the literature: 1.2-100 mg kg^{-1} [Buss et al. 2016], 1-19.41 ng kg^{-1} [Anzano et al. 2017]. This may be to the fact that the most studies have been conducted in a lab-scale experiments and/or different type of feedstock. In our ASR feedstock, significant source of PAHs will be the plastic and rubber fractions (Table 4.2).

Table 4.9 Concentrations of PAHs in produced solid residue (fine char at various temperatures) collected from ASR pilot plant pyrolysis

Target Compounds	**CAS***	**R.T. (min)**	**Char at 800^{o}C (mg kg^{-1})**	**Fit (%)**	**Char at 1000^{o}C (mg kg^{-1})**	**Fit (%)**
Naphthalene	91-20-3	3.23	5010.00	99	46.60	99
Acenaphthylene	208-96-8	4.36	2040.00	99	91.00	99
Acenaphthene	83-32-9	4.48	56.80	73	< 8.00	-
Fluorene	86-73-7	4.87	192.00	99	9.63	97
Phenanthrene	85-01-8	5.72	3980.00	99	429.00	99
Anthracene	120-12-7	5.77	724.00	97	101.00	98
Fluoranthene	206-44-0	7.07	2470.00	89	879.00	90
Pyrene	129-00-0	7.36	2870.00	87	1250.00	88
Benzo[a]anthracene	56-55-3	9.05	401.00	96	93.70	94
Chrysene	218-01-9	9.11	504.00	99	124.00	97
Benzo[b]fluoranthene	205-99-2	10.58	583.00	97	268.00	90
Benzo[k]fluoranthene	207-08-9	10.62	211.00	98	70.30	90
Benzo[a]pyrene	50-32-8	11.01	609.00	97	336.00	96
Indo[1,2,3-cd]pyrene	193-39-5	12.38	496.00	89	451.00	91
Dibenzo[a,h]anthracene	53-70-3	12.41	42.10	85	13.10	72
Benzo[g,h,i]perylene	191-24-2	12.68	524.00	93	627.00	95
Coronene	191-07-1	14.88	136.00	52	285.00	68
Total (USEPA16) PAHs			20712.90		< 4797.33	

Keys: [Chemical abstracts service registry number]*

The occurrence of PCBs and BTEX in the ASR pyrolysis solid residue extracted at various tempertures are presented in Table 4.10. Its obvious that the concentrations of PCBs in the solid residue at 800^{o}C were lower compared to the 1000^{o}C pyrolysis char, which is consistent with the observation by [Conesa et al. 2009] that the dioxin and dioxin-like PCBs concentrations incresaed in pyrolysis product with increasing chlorinated degree and tempertaure process. The total concentrations of PCBs in solid residues produced at 800^{o}C and 1000^{o}C pyrolysis temperetures were < 175.0 μg kg^{-1} and < 508.7 μg kg^{-1}, respectively. These concentrations were higher than the value reported by Joung et al. 2007$_{b}$ of PCBs in the char of 0.869 μg kg^{-1}, however the pyrolysis experiments was carried out in a bench-scale reactor at the temperature of 600^{o}C. Other explanation that this study investigated the solid residue char in fine formation (i.e. exclude coarse-ash contents) compared to the reported literature. On the other hand, the quantities of BTEX drop off dramatically above pyrolysis tempertaure of 1000^{o}C. In descending order, the BTEX with the highest concentratins (in the solid residue of 800^{o}C pyrolysis) were benzene, toluene, xylenes, *m/p*-xylenes, *o*-xylene and ethylbenzene. However, thermal treatment in ASR resulted in an increase of organic pollutant emissions (PCBs and BTEX) compared to feeding material ASR (Table 4.5), the products are not hazardous applied to waste accepted criteria (Table 4.6) and may be safe to be disposed of and/or recycled.

The results of TPHs, TOCs and LOI of the solid residue produced at various pyrolysis temperatures are reported in Figures 4.6 and 4.7, respectively. The TPHs concentrations of the solid residue at 1000^{o}C pyrolysis temperature was significantly lower (a decrease of 67.6%) than 800^{o}C solid residue, with maximum of 36200 mg kg^{-1}. Results obtained for TOC did highlighted no significant differences between solid residues at various temperatures of < 25%wt concentrations. Whereas, values obtained for L.O.I revealed a slight increase concentration in 1000^{o}C solid residue. Based on these results, the values were above the limit to expect hazardous waste to meet the 6% TOC limit set out in the Council Decision (or the 10% LOI limit). This suggests a pretreatment of a raw ASR may necessary perior thermal treatments. Cossu & Lai, (2013) study found that washing teratment of ASR achived removal rates of more than 60% for dissolved organic carbon (DOC) and chemical oxygen demand (COD).

Table 4.10 Concentrations of PCBs (7 congeners) & BTEX in produced solid residue (fine char at various temperatures) collected from ASR pilot plant pyrolysis

Compounds	**Char at 800°C (μg kg^{-1})**	**Char at 1000°C (μg kg^{-1})**
PCB28	< 25.0	59.1
PCB52	< 25.0	87.2
PCB101	< 25.0	53.9
PCB118	< 25.0	< 25.0
PCB153	< 25.0	< 25.0
PCB138	< 25.0	210.9
PCB180	< 25.0	47.6
Benzene	13100	420
Toluene	1220	< 25
Ethylbenzene	167	< 25
Xylenes	855	< 75
m/p-xylenes	679	< 50
o-xylene	176	< 25
MTBE	< 50	< 50

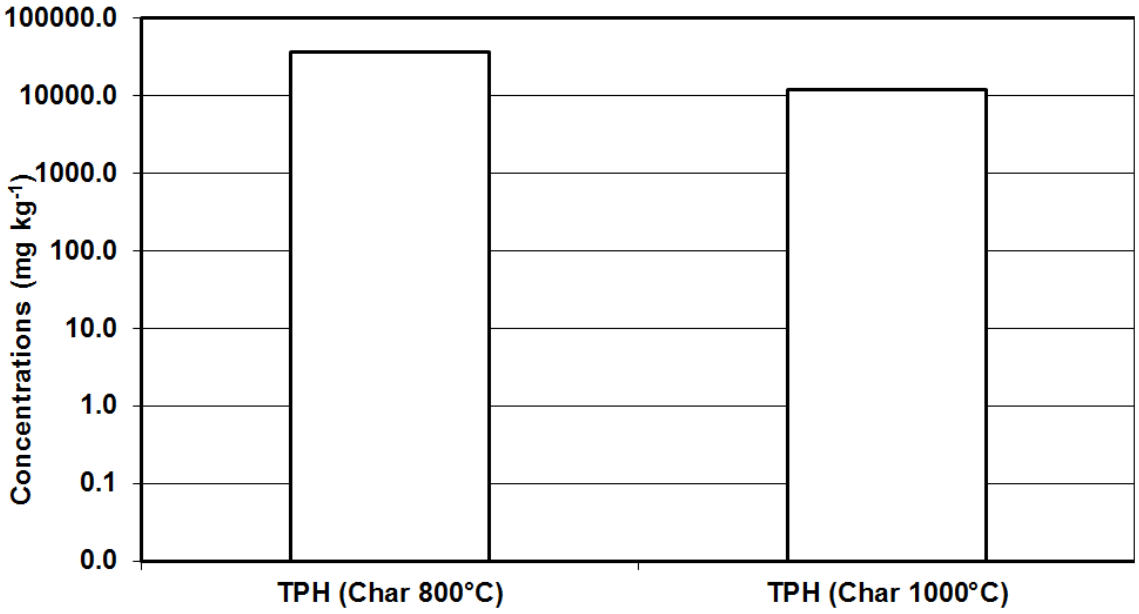


Figure 4.6 Concentrations of TPHs in produced solid residues (fine char at various temperatures) collected from ASR pilot plant pyrolysis

Solid residues 1000°C and 800°C presents significant differences in pH values, since solid residue 1000°C showed slightly neutral pH values (from 7.3) and similar to the pH of the ASR raw feed material of 7.2 (Table 4.5), which means that it will not be a significant leaching of acidic or basic components of the char residues. Solid residue

800ºC have considerably higher pH values of 9.3, which means that it may be a substantial leaching of basic components from the chars.

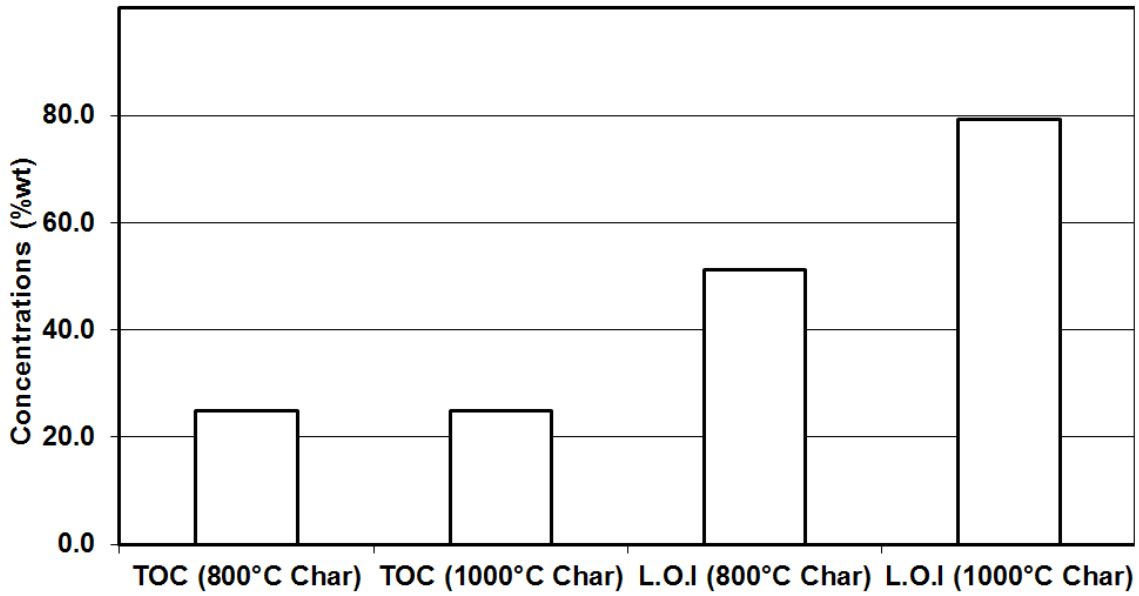


Figure 4.7 Concentrations of TOC & L.O.I in produced solid residues (fine char at various temperatures) collected from ASR pilot plant pyrolysis

4.4 Summary

Summary from this work are presented below for the experimental and commercial parts.

4.4.1 Experimental

- The raw ASR feed material (obtained from UK shredder plant) had gross calorific value range from 16.3-23.4 MJ kg^{-1}. The majority of materials are mixed plastics, which accounted for ~ 47% by weight. The metal content was very low and was combined into the fines (≤ 5 mm). This would indicate that it would make an ideal material for gas production.

- The copper and chlorine contents in the raw ASR were low; this was mainly due to the post-shredder technologies removing both copper and electric cables. This removed the main source of chlorine and catalytic copper so reduced the impact of dioxin/furan production during thermal processes.
- The raw ASR can be classified as non-hazardous waste due to its low contents of hazardous substances such as PCBs, PAHs, BTEX and mineral oil. This means on a commercial plant it can be safely handled.
- The pyrolysis rotary kiln system (temperature ranging from 800-1000^{o}C) performed well with ASR ($\leq$ 20 mm size fraction), producing stable pyrolysis of the materials. This would indicate that any commercial process should aim to operate within this range.
- The CO/CO_2 ratio in the syngas increases slightly with the temperature. Whereas, CH_4 content decreases with the pyrolysis temperatures.
- Benzene, propylene, 1,3-Butadiene, toluene, pentane and o-xylene were the abundant minor gases species identified in the syngas with concentrations of $\leq$ 0.1%vol. This would indicate that the syngas produced having an appreciable energy content can be used for combustion.
- The calorific value of the chars (by-product of pyrolysis) in fine fraction was high in every pyrolysis temperature and it is maximal at 800^{o}C. This has the potential as a separate fuel source.
- Char-coarse calorific value is notably low, therefore it is not viable for energy recovery. However, it may still benefit as a filler in construction material or a secondary source for metals and therefore avoiding landfill. The pyrolysis solid residues could be separated on a commercial scale into heavier organic compounds (fine fraction), recyclable metals/ash waste (coarse fraction) stream for disposal.
- Low levels of PAHs, BTEX and TPHs were found in the solid residues (char-fine) produced at 1000^{o}C compared to the char 800^{o}C. This indicates that to achieve a commercial fuel source the higher processing temperature would be required.

4.4.2 Commercial assessment of the thermal technologies

- Currently, there are no commercial plants, which offer a feasible method for the thermal recovery (pyrolysis and gasification) of ASR. Worldwide there are a number of organisations which have processes, which are claimed can be adapted, but these are yet to be proven. Many commercial organisations assume that their process which takes a homogeneous product can be easily adapted to heterogeneous one. This is not the case and explains the lack of commercial ASR plants.
- Until alternative processes become viable it will be difficult to meet existing legislation without the recovery of ASR. This is a challenge for the EU car manufactures.
- Renewed efforts are necessary to employ alternative pathways for both the technology providers and shredding companies. Only then will a solution provide the access to the principles of the circular economy.

CHAPTER 5 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

5.1 Conclusions

The project met its aim to evaluate and examine the performance of automotive shredder residue (ASR) under thermal treatment technologies.

This work focused initially on the thermal technology industrial plants available worldwide and application of new technologies in the automotive recycling field. The criteria list created for evaluating these technologies supported the view that the technology was applicable. Assessment of the commercial technologies available worldwide revealed that many had not been commercially viable. It also showed that although there were a large number of facilities none of them met the requirements to process ASR. Therefore, there was a commercial need to develop a bespoke solution to the problem of meeting both the ELV Directive and the commercial realities of the recycling sector.

The challenge of recycling end of life vehicles to meet European targets currently rests with the automotive recycling industry rather than the OEM. This means that more material from vehicles needs to be recycled. The Directive 2000/53/CE revised 2015 recycling target states at least 95% by weight of vehicle needs to be recovered. The recycling normally recovers at least 85% by weight, which leaves 15% as ASR. This means that the remaining ASR, which is the non-recyclable fraction, has account for another 10% by mass. This will raise the recoverability rate to 95%. The implication of the EU Directive was that from 2015, only 5% of a vehicle would be allowed to end up in landfill. One potential answer was to recover the energy within the ASR through thermal processing. This study has shown that pyrolysis could be the solution to the biggest challenge in the car shredding industry.

The initial evaluation of ASR composition showed that this was dependent on the recycling industries processing plant. ASR was a very heterogeneous waste and its

material composition still reflected all components found in an ELV. The particulate size of ASR was extremely irregular which makes separation of components difficult. The research showed that depending on the depollution step efficiency of the recycling operator other pollutants such as hydrocarbons, PCBs and mineral oils were present.

The analysis of the ASR at the case study site revealed that polymers represent almost 50% of the total mass and the largest share of the gross calorific value (CVgross). This supports the use of thermo-chemical conversion of ASR. The implication of introducing further PST would be to not only reduce the amount of material going to landfill but to reduce the presence of metals which could be precursors to dioxin production in any thermal treatment process. The case study site illustrated the importance PST by reducing both the copper and chlorine components in ASR.

A series of bench-scale experiments investigated the pyrolysis products of ASR, which confirmed that pre-treatment of ASR was necessary for any correct thermal conversion. The use of a pilot-scale rotary kiln to pyrolyse ASR (from the case study shredder) confirmed that this was a potential commercial solution. The experiments showed that both useful syngas and char by-products were produced. Detailed analysis of the char into two fractions (coarse and fine) intimated their potential as innovative products. This would support higher recovery than the 95% stated in the Directive and it could have important implications for ELV recycling. This benefits the automotive industry by allowing them to achieve the EU and UK targets.

5.2 Suggestions for further work

- To undertake further identification of plastics type in the ASR to help understand both the use of other types of post shredder treatment technology and thermal processes.
- To evaluate the syngas compositions across different operating conditions and in particular amounts of hydrogen produced. This will allow the evolution of splitting the syngas into different fractions for commercial use or the use of catalysts to improve yields.

- To explore the efficiency of the processes using the mass balance of gas, char and liquid fraction under different commercial operating conditions.
- The promising studies on the commercial assessment of the pyrolysis and gasification technologies should be extended to include an assessment of automotive manufacturers current and future role in ELV recycling: including ASR thermal treatment route.

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APPENDICES

APPENDIX A

Reported profile and communications outcome of some worldwide commercial industrial plants or near commercial status for a potential ASR thermal treatment.

Table A.1 List of some deselected companies – gasification industrial plants

- **Deselected**

- Company & Location: BTG Biomass Tec. Group BV, Netherlands
  Private R&D for the past 29 years has specialised in developing processes for conversion biomass into fuels and energy.
  Deselected: reasons that were contacted to gather information, outcome: have the potential to be commercially available within the next 5 years.

- Company & Location: ANDRITZ Carbona, Finland
  Claims to deliver gasifier plants (based on circulating fluidized bed (CFB) & bubbling fluidised bed (BFB) technologies) using woody biomass as feedstock & related systems for power production. Capacity range 10-200 MW/fuel.
  Deselected: reasons that not interested in ASR project & not willing to discuss the company's capabilities & past experience.

- Company & Location: HERLT, Germany
  On business since 1991 on heat generation from straw using close-coupled gasification technologies. Claims capability of supply fully operating plant facilities in Germany, Europe including Ireland.
  Deselected: reasons that this company for the supply of combustion technology rather than gasification.

- Company & Location: TK Energi AS, Denmark
  Claims that their main is gasification of biomass. On their website indicated that they signs billion gasification technology agreement with Royal Dutch Shell. However, I no evidence that the company is currently active.
  Deselected: I received no response to emails and/or telephone number was unobtainable.

- Company & Location: Thermochem, USA
  On business since 1985. Provide chemical testing/services for thermal power plant & energy projects.
  Deselected: Consulting services. However, provided a laboratory analysis.

- Company & Location: T&M, USA
  Provides services for renewable energy. Helping to develop renewable power generation includes engineering construction.
  Deselected: Could not be contacted.

- Company & Location: Organic Power Ltd., Norway No Image
  Plans to commercially deliver renewable energy for power application and/or combined heat & power (CHP).
  Deselected: communication terminated. Mr. MD pointed out was not prepared to discuss the company's capabilities and past experiences any further.

- Company & Location: KN Consult ApS, Denmark No Image

Limited information available of their gasification plants on the website. Web address appears to be redundant. KN's Polish subsidiary (specializes in mechanical engineering activities) seems took over.
Deselected: Polish subsidiary showed limited experience in gasification equipment.

- Company & Location: Grubl Automatisierungstechnik GmbH, Austria
Claimed that the produces wood gasifiers for heat & electric power (5-100 kWe). Larger scale under construction supported by the government.
Deselected: I received no response to emails and/or telephone number was unobtainable.

- Company & Location: Global Olivine, UK
Company goal to work in partnership with government, businesses to deliver sustainable solutions to energy from waste. Attempted to develop a renewable energy project in Peterborough, UK but the project was abandoned.
Deselected: Company showed limited experience in biomass treatment.

- Company & Location: Foster Wheeler, UK, Finland
Company Finland branch has proven biomass gasification technology plants in Scandinavia & application for syngas (includes injected directly into the adjacent power plants).
Deselected: Company interested in large scale plants /projects only.

- Company & Location: Future Energy GmbH, Germany
Claimed of gasification experience more than 30 years. Research projects of straw gasification with University of Karlsruhe.
Deselected: Company showed limited experience in biomass treatment. It looks like their gasification experience in coal rather than biomass.

- Company & Location: ENER-G, UK
On Business since 1992. Experienced on combined heat & power (CHP) projects. Developed a small scale packaged fast pyrolysis system.
Deselected: Company appears to be interested on biomass combustion rather than waste/biomass gasification.

- Company & Location: Cratech Inc., USA
Claimed to develop a patented biomass/waste power plant system. However, very limited information available on their website. It seems like a small company with a low experience in the whole gasification equipment.
Deselected: In communicate with Mr. Founder/President, it was difficult to compete against gasification plant of ASR requirement and I have not received any response of the process.

- Company & Location: Cosmo Powertech PVT, India No Image
Claimed that they capable of development & design biomass/waste gasifiers (updraft & downdraft). Capacity range up to 35MW_{th}.
Deselected: The company currently does not offer any gasification processes.

Mr. MD said that they are working on development of waste gasification technology ready for commercial offer within 1-2 years**.**

- Company & Location: Bio-flame, UK
  Located in north Yorkshire involved in design, construction & deliver waste to energy systems includes various feedstock. Systems capacity up to 1 MW_{th}.
  Deselected: reasons that this company for the supply of combustion technology rather than gasification.

No Image

- Company & Location: CCT (Caldareria Costruzioni Thermomeccaniche S.R.I.)
  Offers gasification plants for waste/biomass (e.g. RDF) with power & heat generation. No clear information/data on the website.
  Deselected: from the communication, I was not able to clarify whether the company involved in the design/operation of gasification units or worked as a third party to others with no experience in the gasification systems. Therefore, I have not considered them further.

- Company & Location: Chemrec, Sweden
  20 years of experience in the field of black liquor gasification technology. Capacity A300 Booster gasifier (150-300 t/d), OX450 Booster (450 t/d), P500 Expansion unit (500-550 t/d), P2000 replacement unit (1000-4000 t/d), X2000 combined cycle unit (1000-4000 t/d).
  Deselected: reasons that the company concentrating on the black liquor gasification only.

- Company & Location: B9 Energy, UK
  On business since 1992. Support/developing renewable energy projects.
  Deselected: Consulting services.

- Company & Location: Balboa Pacific Corporation, USA
  On Business since 1991. Developed the Bal-Pac gasification system able of continuous feedstock wastes (solid or liquid).
  Deselected: Communication forced by them into one direction which is a feasibility study (cost between $65,000 – 95,000 plus expenses (e.g. accommodation, transportation)). They will send a qualified engineer & waste management specialist to the project site (between 5-7 days) where then prepare a report. 50% of the feasibility study fee required to be deposited prior to the expected arrival date.

- Company & Location: Chinook Science, UK
  Claims that they developed a combining pyrolysis and gasification RODECS® system (1st system was commissioned in 2000). Also, the system able to monitors & conditions the syngas during the processing cycle. Altering the gaseous composition & the atmospheric conditions according to the target requirements. Small to large capacity units available.
  Deselected: I received no response to emails and/or telephone number was unobtainable.

- Company & Location: Klean Industries, Canada

Offers design, manufacture and installation of advanced thermal treatment. Raw material: all types of plastics (include mixed plastic PVC 20% by weight), ASR, scrap tyres, biomass, infection biohazard medical waste, MSW. Klean-Industries planning out facilities in North America & Europe that incorporate the same proven SPR technology in Japan (capacity (50 t/d).
Deselected: Communication forced by them into one direction which is a feasibility study/detailed quotation (cost $4500).

Table A.2 List of some advertise pyrolysis industrial plant – plastic feedstock

- **Plastic to Oil Plant**

- Company & Location: PYROCRAT, Mumbai, India
Capacity (3 t/d, 6 t/d, 12 t/d, 24 t/d, 48 t/day). Raw material: Mixed plastic, carry bags, bottles, mixed plastic scrap, laminates, packing material waste, plastic waste from paper recycling mill, multilayered plastic. Production cost of less than USD 0.22 per litre of Pyrolysis oil. Up 95% conversion of waste plastic into pyrolysis oil.

- Company & Location: Cynar PLC, London, UK
Capacity (10 t/d & 20 t/d). Raw material: Plastics (HDPE, LDPE, PP, PS). None-acceptable plastic feedstock includes; PET, PVC, foams, nylon and fiberglass. Heating non-recycled plastic in the absence of oxygen to around 400-500°C. CynFuels consisting of around 70% diesel, 20% light oil and 10% kerosene. The syngas produced in the process is recycled to heat the pyrolysis pots. 5% residual char can be sold on (e.g. make briquettes for kiln firing). Cynar challenges the ability to use plastic-heavily contaminated farm.

- Company & Location: Biogreen, France
Capacity (bench type 30 m^3/h to industrial plant up to 7.5 m^3/h). Raw material: Waste plastics (such as car fluff/frag). Oil yield up to 50%, chare 5 – 30%. (In term of gasification up to 80%). Biogreen technology based on Electric heating. Electrical consumption 50-200 kWh/t of inlet product. Limitation: low moisture content feedstock (< 8%) & particle size < 20 mm required. Cost: 800,0000€ for a 2.5 m^3/h to 2.2 M€ for a 7.5 m^3/h. Own product can be tested on Biogreen Bench type.

- Company & Location: Klean Industries, Canada
Carbonizing (for carbon pellets) & pyrolysis plant of waste plastics. Raw material: all types of plastics, ASR, scrap tyres, biomass, infection biohazard medical waste, MSW. Klean-Industries planning out facilities in North America & Europe that incorporate the same proven SPR technology in Japan (capacity (50 t/day), Raw material: Mixed plastic, (include PVC 20% by weight). Technology has patented dechlorination process that removes hydrochloric gas

produced by thermal decomposition of PVC and uses water to convert gas into hydrochloric acid leaving only 100 ppm of Cl in oil product. High quality oil recovered. 4MW_e of electricity to the grid).

- Company & Location: Shree Balaji Engineering Works, India
  Capacity (6, 10, 15, 20 t/d), Raw material: Waste plastic & Tyres. Technology features: robust construction, low maintenance, high performance, longer service life.

- Company & Location: Get Energy Prime, Italy
  Capacity (200 – 1000 kg h^{-1}), Raw material: Plastics (max. % of PVC permitted 2-3 %), Tyres (ELTs). Feed size 10 – 35 mm (need a bit of washing treatment before putting into the shredder machinery). Production 85% oil-diesel, 10% gas recovered inside the system for additional electricity production, 5% inert residue.

- Company & Location: EPi, Environmental Power International Ltd, UK
  Capacity (N/A), Raw material: Plastic, MSW, medical waste. A typical installation of six Epi modules has the capability of producing more than 7 MW hour electrical, 10-15 MW hour thermal. Use of carbon char a further commercial opportunity.

- Company & Location: BESTON, China
  Capacity (have 3 models (WJ-6, WJ-8, WJ-9. 6 – 20 t/d). Raw material: Mixed plastic. Oil yield 50–70% from PE, PP & PS, 40% from ABS. Plastic need to be cut into 30–50 mm. if water percentage of plastic more than 215%, then need to be dried.

- Company & Location: Huayin Group, China
  Capacity (3-10 t/Batch). Raw material: Plastic, PP, PE, PS, ABS, rubber, medical waste, MSW. Adding into heavy oil generator to produce electricity. Temperature of 400-450°C. Oil yield 50-75%.

- Company & Location: Doing Energy, China
  Capacity (6/8/10 t/day). Raw material: waste plastic. Temperature of 350 to 460°C. Oil yield (N/A).

- Company & Location: RESEM, Taiwan
  Capacity (5/8/10 t/d). Raw material: Mixed plastic (PE, PP, PS, ABS, HDPE, LDPE, Nylon), mixed waste plastic from waste paper mill, plastic or rubber parts from vehicles. Temperature 250°C. Oil yield (N/A). Delivery time 20 days.

- Company & Location: Oorja Systems & Consultants, India
  Capacity (1-10 t/d), batch type conversion (6-8 hr). Raw material: Plastic. Oil yield 50–75%, gas 20-30%, char 5 -20%.

- Company & Location: PPP, Canada

Capacity (N/A), Raw material: Scrap Plastics. Production high grade diesel fuel.

- Company & Location: Conversion & Resource Evaluation Ltd, UK
Capacity (design & build lab, pilot to commercial scale (5 kg/hr to 6 t/d fluid fast pyrolysis plant)). Providing technical & economical services in waste conversion sector.

- **Plastic to Electricity Plant**

- Company & Location: PYROCRAT, Mumbai, India
Capacity (3 t/d, 6 t/d, 12 t/day, 24 t/d, 48 t/d), Raw material: mixed plastic, carry bags, bottles, mixed plastic scrap, laminates, packing material waste, plastic waste from paper recycling mill, multilayered plastic. Production cost of less than USD 0.22 per litre of Pyrolysis oil. Electricity generation capacity of 0.25 MW to 5 MW per hour.

- Company & Location: Splainex, Netherlands
Capacity (9t/h), Raw material: Plastics/ASR, biomass, medical waste, tyres. Oil for diesel generators. ASR with LHV = 21 MJ kg^{-1} & 20% moisture can generate more than 10 MW_e. Supply & services; waste preparation (presorting, shredder, dryer) as required, pyrolysis unit, gas cleaning unit, turbines/generator set, internal ducts & stack, pipes & fitting, electrical/process measuring & control equipment, technical documentation, training of operating staff during commissioning.

- Company & Location: Anergy Ltd, London, UK
Capacity (small to medium scale renewable energy power plant), Raw material: Plastic, waste, biomass. 1-10 MW_e production.

APPENDIX B

Examples of mass spectrum of the syngas minor species obtained from ASR pyrolysis pilot-scale trials.

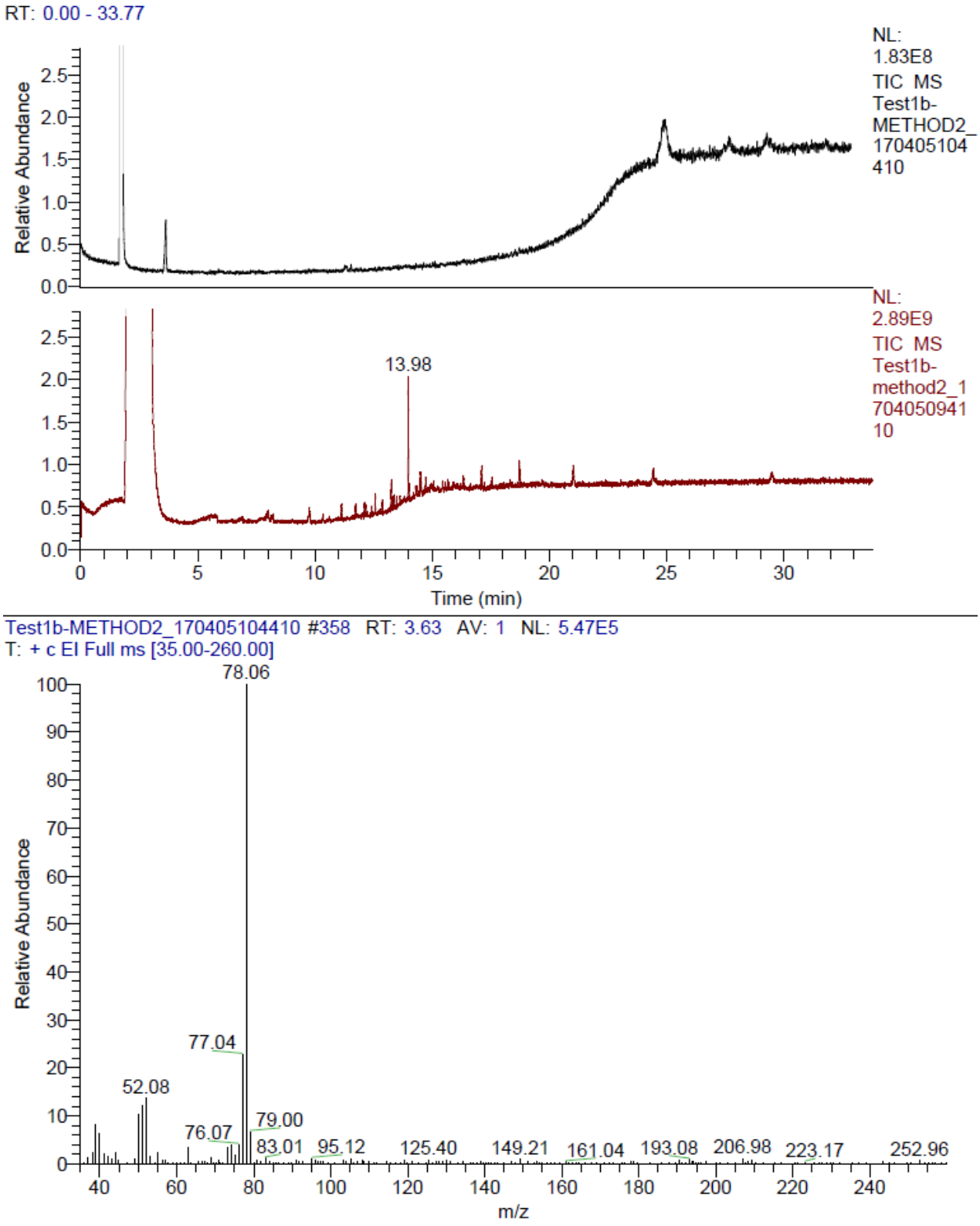

Figure B.1 Mass spectrum of benzene in the syngas produced from the ASR pyrolysis trials identified by GC-MS

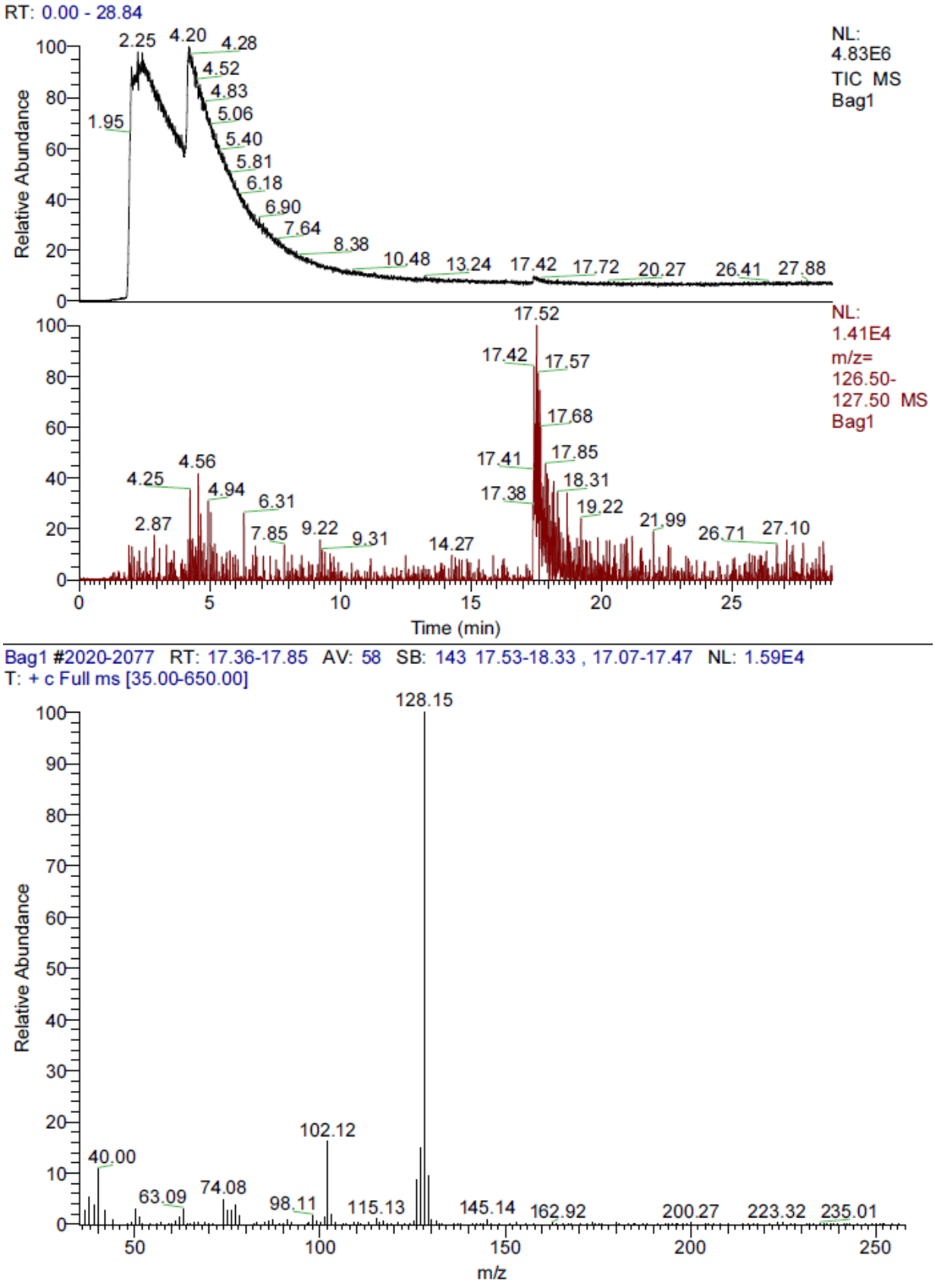

Figure B.2 Mass spectrum of azulene in the syngas produced from the ASR pyrolysis trials identified by GC-MS

APPENDIX C

Images of the solid residue (char) in their two fractions produced from ASR pyrolysis pilot-scale trials. Also, an example of multi-elements standard calibration for quality assurance (QA) using ICP-MS analytical methods as well as formula used to calculate metals concentrations in the samples.

Figure C.1 Close-up view of the pyrolysis solid residue (char) by-product. (a) Fine; (b) Coarse

C.1 Calculation of the metals concentrations

10 ml nitric acid (HNO_3) was added to each raw ASR or char samples (weight of sample of 0.1 g) and then subjected to microwave digestion. Volume of the extract dilution 1/100 (100 µl digested sample in 10,000 µl deionised water). Extract solutions were centrifuged at 1000 rpm for 5 min at 4^{o}C prior ICP-MS analysis. Three replicates were prepared for each sample.

The concentration of the metals was calculated as follows:

Xc (ppm) = Instrument results*Dilution factor*Digestion volume (µl)/Sample mass (g)

Table C.1 Calibration data for ICP-MS analytical method using multi-elements standards

Run	Time	7Li	9Be	23Na	24Mg	27Al	39K	44Ca	47Ti	51V	52Cr	55Mn	56Fe	59Co	60Ni	65Cu	66Zn	69Ga	85Rb	88Sr	95Mo	103Rh	107Ag	111Cd	115In	133Cs	137Ba	208Pb	209B
		Blank	13/10/2017 16:00:37																										
1	16:00:48	1492.122	16	906735.3	3040.508	3792.791	452218.6	2.2808.83	108.001	96.001	1140.072	2512.347	2346703.3	184.002	64	232.003	2184.262	16	208.002	360.007	108.001	4	44	8	268.004	2540.355	0	228.003	448.011
2	16:00:59	1356.086	20	905201.1	3200.563	3528.685	450302.2	2.2357.97	132.001	92	1204.08	2544.356	2329417	232.003	52	248.003	2368.308	20	172.002	376.008	140.001	0	68	4	324.006	2528.352	12	320.006	376.008
3	16:01:10	1432.113	0	897437	3092.526	3656.735	453311.2	2.2993.04	112.001	88	1352.101	2456.332	2322288	152.001	72	224.003	2180.261	12	244.003	304.005	92	0	56	0	284.004	2568.363	12	260.004	472.012
x		1400.111	12	903124.5	3111.199	3659.404	451244	2.2986.61	117.334	92	1232.084	2504.345	2323281.6	189.335	62.667	234.67	2244.277	16	208.002	346.673	113.334	1.333	56	4	292.005	2546.69	8	269.337	432.01
s		78.701	10.583	4984.856	81.645	132.073	1009.916	238.744	12.858	4	108.753	44.554	1255.336	40.167	10.067	12.221	107.433	4	36.001	37.808	24.441	2.309	12	4	28.845	20.532	6.928	46.706	49.962
%RSD		5.542	88.192	0.552	2.624	3.609	0.224	1.034	10.959	4.348	8.827	1.779	0.538	21.167	16.064	5.208	4.787	25	17.308	10.906	21.565	173.205	21.429	100	9.878	0.807	86.603	17.341	11.565
		62.5ppb std	13/10/2017 16:03:19																										
1	16:03:30	103824.4	23483.77	3218337	192656	199955.1	819351.3	9691788	104.001	250841.6	2258347	412565.9	3382578	2558313	11647.46	13341.78	10766.37	300522.5	295506	4732033	78804.08	12	171209.2	3856.818	6593826	106747.1	152803.83	43021.56	746635.1
2	16:03:40	105164.8	23053.19	3201694	190327.7	195091.1	795027.4	9714023	156.001	245457.6	2262365	404081.2	3287781	2484821	10870.15	13902.62	10662.25	299365.2	2894023	4693385	76996.69	40	171653.4	4288.011	6730365	109297.1	155015.21	44573	736888.8
3	16:03:52	103016.4	22138.92	3167668	187420.2	197179.4	847943.3	9686937	112.001	240976	2227438	4044407	3300027	2486671	11383.02	13650.24	10357.9	299745.5	2947153	467272	78715.32	16	171931.2	3812.799	6539718	108899.9	153812.92	46587.06	742708.2
x		104668.5	22558.63	3195900	191134.7	197408.6	823774.6	9697583	124.001	245758.4	2249383	4070293	3323462	2509875	11273.66	13631.55	10595.51	299877.7	2932111.2	4699379	78172.03	22.667	171964.6	3986.21	6621133	108301.4	153729.9	44727.21	742080.7
s		1468.297	461.708	25826.71	2623.212	2440.072	26486.66	144.432	28	4939.647	1911.095	4798.2	51560.62	4180.293	389.312	280.887	212.259	589.858	3321.622	3010.744	1018.84	15.144	950.026	263.156	9831.63	1363.688	117.433	1787.749	4898.401
%RSD		1.403	2.047	0.808	1.38	1.236	3.227	0.149	22.581	2.01	0.85	1.179	1.551	1.666	3.453	2.061	2.003	0.197	1.133	0.641	1.303	66.811	0.552	6.602	1.485	1.259	0.764	3.997	0.66
		125ppb std	13/10/2017 16:05:58																										
1	16:06:10	187391.7	40361.4	5097276	3002497	356616.1	3564745	1524231.3	128.001	4585659.2	4112103.5	7525021.5	5877200	4635148	28627.38	25455.59	19035.91	5745732	5448085.8	875914	1446213	48	3231956.8	7238.881	1281985	2017828	28958.05	85605.17	1489060
2	16:06:20	184668.8	41647.18	5167125	3007705	3578055	3587516	1559866	124.001	4601612.8	4213095	7708266	6052446	4738518	20647.42	26285.95	19969.91	5647026	5687934.2	902706.4	1472916	28	3189838	7350.971	1271774	209257	29744.58	89017.71	1452990
3	16:06:32	190830.1	40542.2	5032727	2937835	3535019	3561614	1536231	160.001	4594548	4116411.4	7709959	6020888	4719358	20406.88	24944.55	19063.97	5605043.2	5552374.4	898800.2	1483242	52	3171887.6	7539.125	1235228	203022	28504.62	87701	1487487
x		187639.2	40850.26	5097891	2982679	3559745	3571292	1540138	137.334	4579892.6	4163105	7647754	5983511	4694868	20560.56	25362.03	19356.6	5664396	5662791.1	893480.2	1467457	42.667	3199556	7376.325	1262962	2046872	29069.08	87441.29	1476512
s		3087.568	696.048	68939.47	3892.322	2222.354	14137.53	1809.68	19.732	6573.498	5050.261	10628.57	93410.38	5352.603	133.467	974.073	531.331	7419.109	12028.08	1447.77	1910.885	12.858	2880.398	151.719	24545.15	4005.698	627.394	1721.03	2083.84
%RSD		1.646	1.704	1.352	1.305	0.624	0.396	1.175	14.368	0.584	1.213	1.39	1.561	1.14	0.649	3.841	2.745	1.31	2.162	1.622	1.302	30.136	0.9	2.057	1.943	1.957	2.158	1.968	1.381
		250ppb std	13/10/2017 16:08:38																										
1	16:08:49	341035	75141.26	8659221	5708662	676073.9	6370533	2721202.7	396.002	8908233.6	7695791	1479752	11111062	8846238	38328.63	47427.39	36183.87	1076661	1077503	1493247	2744615	60	6245147	13293.71	2324325	388971.1	55339.93	159685	2614999
2	16:09:00	348091	75955.99	8757074	5662803	6556697	6443240	2685351.1	160.001	8835726.6	7621768	1471855	10717518	8809417	38123.77	47266.56	36027.25	1051731	1078208	1468321	2662552.9	88	6266504.1	14171.04	2050670	3891381	54949.57	159253	
3	16:09:11	357472.8	76456.16	8833862	5711641	664665	6436648	2758424	116.001	9004547	7953106	1441191	11135695	8809983	38915.11	46780.05	36987.09	1119428	1083465	1538820	2734064	76	6319364	14771.99	2129065	3771149	56164.96	169884.7	2972599
x		348866.3	75851.44	8770052	5694369	665479.5	6441687	2721104.7	157.335	8916156.9	7756588.8	1464266	10988758	8848898.8	38455.84	47158	36399.4	1080607	1079725	1571329	2713564.6	74.667	6277039.7	14078.31	2168020	3850747	54684.82	162351.7	2833367
s		8246.256	663.689	78133.01	2737.712	10211.5	40209.57	3745.668	40.067	8468.968	17391.35	20369.89	2351724	4082.073	410.722	337.048	514.943	349237.38	3257.913	98448.92	4481.379	14.098	3835.954	743.433	14925	6893.873	620.517	6524.473	1914844
%RSD		2.364	0.875	0.891	0.481	1.534	0.627	1.377	25.466	0.95	2.242	1.391	2.14	0.461	1.068	0.715	1.445	3.232	0.302	6.265	1.651	18.814	0.611	5.28	6.5	1.79	1.118	4.019	6.758
		500ppb std	13/10/2017 16:11:18																										
1	16:11:30	632349.4	136229.1	15234845	10043383	1169245	10886042	4688776	116.001	14153101	14003647	4884677	19807716	16237708	67558.1	85968.57	62659.2	1956225	1686721	3221171	5236048	92	1168982	23839.22	4380625	7038001	97981.19	273955.8	5203448
2	16:11:41	641500.7	137113355	10277822	10268833	1173337	10906626	4684002	184.002	14353728	14832323	2594302	21166456	16579726	74762.16	89938.7	66832.76	2172801	1788111	3255966	5338102	176.002	1214270	26161.59	4559853	7476323	1080787	308159.9	5612921
3	16:11:52	645644.9	139372.2	15459423	10323954	1188016	11293221	4928088	148.001	13380615	14830862	3392833.2	20613273	15522221	70077.06	87038.68	65640.12	1902944	2002359	3302544	5153654	104.001	1206503	26245.83	4401412	7254248	105796	313986.3	5480673
x		645268.9	138034	15458541	10217201	1195048	11304190	4867709	149.335	14563464	14838047	3404984	20529149	16109185	70799.1	87648.65	65944.08	2010657	1829063	3259894	5241935	124.001	1196585	25415.55	4447297	7256191	103952	288714	5432347
s		12735.67	2652.029	209776	15231.88	29288.62	42739.3	23464.32	34.02	162764.2	42035.48	12610.78	683255	53548.26	3655.904	2054.152	2149.688	142925.7	1600715	40828.08	9136.606	45.432	24218.08	1365.791	98029.32	21916.71	5295.3	21663.92	208969.9
%RSD		1.974	1.907	1.354	1.491	2.451	3.749	4.82	22.781	11.176	2.924	110.554	3.328	5.164	2.344	3.305	7.108	8.752	1.252	1.743	36.638	2.024	5.374	2.204	3.02	5.094	7.352	3.847	
		1000ppb std	13/10/2017 16:13:59																										
1	16:14:10	851506.4	255607.6	28103442	9862227	1481793.3	20676504	8663634.3	244.003	28873338	25595080	4768472	38083702	30034431	126713	160024.1	119530	3676463	3744476	6047715	9742844	212.002	2147406	43073.8	8397346	1396656	1928153	547050.8	9998896
2	16:14:21	915354.2	261771.3	29016153	11903387	1617218	21577008	8983888.8	156.001	29624422	26208066	4854771	38827757	30919767	126299.3	164767.8	117312.1	3676592	3801798	6000998	1009399	264.004	2298251	45618.17	8604550	1404210	1932161.9	551266.4	10407113
3	16:14:32	931284.8	259985.2	28429988	12718888	1588019.4	22066151	8837117	144.001	29674401	26510559	4929858	38773169	30596509	126469.6	165802.3	122039.9	3683487	3817729	6029035	1021140	260.004	2358492	47105.73	8527330	1420270	1948337	564256.1	10442048
x		899381.8	259124.4	28516528	11493501	1610511.5	21072255	8812465.9	181.335	29390654	26223515	4851034	38561543	30277273	126404	163531.4	119715.3	3676847	3787001	6025916	1010608	245.337	2288050	45265.9	8509742	1407045	193337	554191.1	10382686
s		42219.5	3171.35	46246863	1471543	166216.8	1603229	165162.42	54.603	448562.02	2832838	80758.04	4147215.5	283382.5	207.92	3081.111	2447.021	4019.027	40222.15	235151.81	24380.31	28.937	108735.9	2038.915	104715.6	12659.29	1315.879	8967.782	24638.9
%RSD		4.694	1.224	1.622	12.802	51.92	2.184	1.874	30.112	1.526	1.08	1.665	1.075	0.936	0.164	1.884	2.044	0.109	1.062	0.39	2.494	11.795	4.794	4.504	4.235.9	1.231	0.857	0.681	1.618	2.396
		Sample 1	13/10/2017 16:16:40																										
1	16:16:51	9809.289	124.001	2596182	2498133	1490062.5	1082352	2454602	6382.239	16707												4.183	1080.064	14615.58	252.003	1987.3	2952.479	1029966	360942.8	164987.7
2	16:17:02	9813.294	80	2617398	2492328	1478991.9	1072191	3164201.5	6138.072	16334												0.152	972.052	14882.19	328.006	19985.29	2828.44	1003069	374443.8	162782.6
3	16:17:13	9432.891	112.001	2580354	2458432	1464686.5	1072101	2409032	6038.005	15605												6.126	848.04	14299.24	396.009	18546.9	2728.409	1009921	376193.9	159439.8
x		9685.158	105.334	2597978	2482328	1476136	1077548	2686865	6186.105	16215												6.126	966.719	14569	325.339	19368.63	2836.443	1034318	376268.9	162403.4
s		218.479	22.745	18587.11	21426.67	24785.7	3892.482	1221537	177.073	560.1												4.137	116.104	300.064	72.04	717.847	112.249	13977.29	8690.612	2799.301
%RSD		2.256	21.593	0.715	0.863	1.7	0.548	70.745	2.862	3.4												9.247	12.01	2.06	22.143	3.706	3.957	1.378	2.347	1.724
		Sample 2	13/10/2017 16:19:22																										
1	16:19:33	5261.522	52	78763.73	5789885	7482115	1031145	1154001	7423.029	2602												2.325	156.001	5829.869	348.007	14275.2	2648.386	1949380.8	175942.8	233931.6
2	16:19:44	5325.559	36	59791.99	9770243	7495753	1011231	1172023	6674.449	2582												6.458	132.001	5405.607	372.008	14211.1	2252.279	1902115	180775.7	237605
3	16:19:56	5269.527	40	123655.3	5571705	7752473	1022916	1131489	7310.939	2684.7												4.538	140.001	5857.887	344.007	14331.29	2628.38	195561	184921.9	238695.9
x		5285.536	42.667	87403.67	7049394	7576780	1021764	1152505	7136.139	2624.1												11.107	142.668	5697.787	354.674	14272.53	2509.682	1935878	180346.8	236677.5
s		34.892	8.327	36796.61	2365563	152306.8	10006.7	20308.16	403.744	531.6												17.747	12.22	253.423	15.144	60.139	223.141	2929.664	4803.891	2491.399
%RSD		0.66	19.516	37.523	33.555	2.01	0.979	1.762	5.658	2.0												2.218	8.566	4.448	4.27	0.421	8.891	1.513	2.664	1.022
		Sample 3	13/10/2017 16:22:04																										
1	16:22:15	4541.134	44	29612.4	1246169	9469608	7406317	857439	6550.359	13297												6.348	172.002	7663.229	136.001	5185.479	2452.331	134808.2	120947.4	231547.7
2	16:22:26	4669.199	20	17785.9	1268583	9388505	7432949	835800.4	6218.126	13566												24.35	172.002	7699.092	176.002	5189.481	2396.316	136241.3	125938.1	234243.5
3	16:22:37	4269.002	12	23629.6	1439728	9317219	7481313.6	8486313.8	5085.422	13842												0.349	152.001	7699.092	108.001	5381.592	2380.312	136078.9	125106.3	237917
x		4493.112	25.333	23678.3	1318160	9391777	7439944	847284.4	5951.302	13568												0.349	165.335	7553.804	140.001	5252.184	2409.653	135795.5	125123.9	234569.4
s		204.375	16.653	59182.32	1038757	76246.84	3801.006	10880.42	768.054	272.4												4.001	11.547	94.764	34.177	112.089	37.817	784.747	4433.146	3197.149
%RSD		4.549	65.737	24.994	8.032	0.812	0.511	1.284	12.906	2.0												0.159	6.984	1.255	24.412	2.134	1.569	0.578	3.543	1.363

APPENDIX D

List of publications already published (article, oral, poster) and article submitted to journals from this project.

ARTICLES

[1] Ala Khodier, Karl Williams, Neil Dallison. (2018). Challenges around automotive shredder residue production and disposal. Waste Management, V., 73, 566-573.

[2] Ala Khodier, Karl S Williams, Neil Dallison. (2017). Pilot-scale thermal treatment of automotive shredder residue: Pyrolysis char is a resource or waste. WIT Transaction on Ecology & the Environment, WIT Press, Energy & Sustainability VII, V., 224, 439-450. www.witpress.com,ISSN1746-448X

[3] Ala Khodier, Karl S. Williams, Neil Dallison. (2016). Challenges around automotive shredder residue production and disposal. The Proceedings of the Sixth International Symposium on Energy from Biomass and Waste, 14-17 November 2016, Venice, Italy.

[4] *Submitted to Journal of Analytical & Applied Pyrolysis*, Ala Khodier, Karl S Williams, Neil Dallison. Pilot-scale pyrolysis automotive shredder residue: Investigation of PAHs, PCBs and environmental contaminants in the solid products.

PRESENTAIONS

[1] Ala Khodier, Karl S Williams, Neil Dallison. (2017). Pilot-scale thermal treatment of automotive shredder residue: Pyrolysis char is a resource or waste. Seventh International Symposium on Energy and Sustainability, 20-22 September 2017, Seville, Spain.

POSTERS

[1] Ala Khodier, Karl S. Williams, Neil Dallison. (2016). Challenges around automotive shredder residue production and disposal. Sixth International Symposium on Energy from Biomass and Waste, 14-17 November 2016, Venice, Italy.